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Powell

A study of the forms in which sulfur  
occurs in coal.



A STUDY OF THE FORMS IN WHICH SULFUR  
OCCURS IN COAL

BY

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THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1918



1918  
P87

UNIVERSITY OF ILLINOIS  
THE GRADUATE SCHOOL

May 1, 1918

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPER-  
VISION BY Alfred Richard Powell  
ENTITLED A Study of the Forms in which Sulfur Occurs in  
Coal.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE  
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### Acknowledgment

This investigation was carried on in the Chemical Laboratory of the University of Illinois during the years 1915 - 1918. It was undertaken at the suggestion of Professor S. W. Parr and carried out under his direction.

The writer takes this opportunity to express his most sincere thanks and appreciation to Professor Parr for the very valuable help and direction he has given in connection with the present investigation.

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## THE CONSTITUTION OF COAL.

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Introduction.

The composition of coal has long been a subject of earnest study by many scientists. However, it may be said that no light has been thrown as yet on the exact nature of the principal compounds comprising the coal because of their apparent remarkable complexity.

The methods which have been used in attacking the problem may be divided, in a general way, into three classes. The first is a study of the method of formation of coal, including the nature of the substances from which it was formed. The second class of methods is actual experimental work on the destructive distillation of coal by heat, and the determination of characteristic substances in the distillate. The third class is also one of experimental means, and includes the various attempts to isolate component portions of the coal by the use of solvents.





## Historical

The process which coal has undergone during its formation has shed an important light on the general character of coal composition, but no definite conclusions may be drawn, since the chemical changes involved vary under different conditions and are obscure in all cases.

It is conceded by practically everyone that coal had its origin in vast beds of vegetable matter, supplemented in most cases by more or less animal remains. Several reasons may be advanced as proof of the vegetable origin of coal, the most important of which is the almost universal presence of plant outlines on coal surfaces. Morphological proofs of the presence of animal residues are not so plentiful, but outlines of the skeletons of fishes are often found, which also indicate the presence of water during the early stages. Another very good indication of animal remains in the coal is found by a comparison of the nitrogen content of coal with that of pure vegetable fossils sometimes found in the same general locality. In such cases the coal contains several times as much nitrogen as the vegetable remains, which undoubtedly shows the presence of animal matter in the coal.<sup>1</sup>

The beds of vegetable matter referred to accumulate during long periods of time and complete oxidation of the organic matter is prevented by layers of earthy material. The chemical composition of the original plant material was closely related to that of cellulose, with varying amounts of mineral matter and quite a large amount of water present, also. This vegetable



sphagnum passes over into peat by a process of slow decay. The chemical changes involved during this transformation are typical of a certain kind of bacterial cellulose decomposition, the products of which are the so-called humus substances, such as humic, ulmic, crenic, and apocrenic acids. None of these products are definite chemical compounds and represent merely a type of substance. Because of the acidic character of peat, we find that an alkaline solution will dissolve nearly all of it. Underground waters carry to the peat lime and iron salts in solution. This causes the formation of insoluble calcium and iron salts of the above named acids, so that, although calcium and iron are found in the ash of peat, the calcium hardly ever exists as the carbonate, as might be expected.<sup>2</sup> The change from vegetable matter to peat is accompanied by loss of water and also of oxygen, so that the net result is a gain in the carbon content and a loss of both hydrogen and oxygen. Also it might be mentioned here that each step in the process from peat to anthracite coal involves the same result - a continual increase in the percentage of carbon, a decrease in the percentage of hydrogen and a decrease of oxygen until nearly all of the oxygen has disappeared.

From peat the next step is to the lignites. These are soft, generally brownish-colored deposits, and form the connecting link between the distinctly vegetable peat and the rock-like bituminous coal. Lignites contain organic sulfur as well as pyrites or marcasite and sulfates such as gypsum.<sup>3</sup>

The changes from lignites to bituminous coal and thence to anthracite coal give no characteristic indications whereby we could deduce much concerning the composition of the coal, except





perhaps the tendency to approach nearer and nearer to a hydrocarbon. The earlier chemical changes are largely bio-chemical, while the latter are more distinctly dynamo-chemical.<sup>4</sup>

Nearly all of the foregoing matter refers to the chemistry of carbon, hydrogen and oxygen in the coal. The methods of formation of the nitrogen and sulfur compounds have also their significance in the question of how these elements may be combined in the coal. As stated before, a large part of the nitrogen of the coal comes from the remains of animals, and since all the rest comes from the plant substance, it must exist in the coal as organic amino nitrogen, unless, indeed, there have been nitrifying bacteria present to cause oxidation.

The sulfur of the coal may come from two entirely different sources. The original plant and animal substances out of which the coal was formed undoubtedly contained organic sulfur. We do not know whether this organic sulfur changes or not during the coal making process, but there is evidence that it may furnish the sulfur for the pyrites and marcasite of the coal. Furthermore, under the changes occurring in peat, there has been mentioned the fact that iron and calcium are precipitated from ground waters by the humus acids of the peat, hydrogen sulfide waters percolating through the coal substance would change the iron to the sulfide and thence to pyrites or marcasite. It is very seldom that much sulfur in the form of sulfates is found in coal. However, where aerated water has the chance to come in contact with pyrites, a very slow oxidation occurs.

Winchell<sup>5</sup> states that he tested this by having aerated water act on pyrites. At the end of one month, no iron or sul-





fur had gone into solution. At the end of ten months, 0.2 g. of pyrites had been oxidized and he found in the solution 27.7 mg. of ferric sulfate and 5.7 mg. of sulfuric acid per liter with traces of ferrous salts and sulfur dioxide. This shows that it is very possible for comparatively large quantities of sulfate to be formed in the coal, provided the flow of the aerated water is not such as to leach out the compounds as fast as they are formed. Of course, any sulfate formed would tend to go to calcium sulfate or another sulfate not so soluble as the ferric salt.

It has also been found that alkaline waters would decompose pyrite and marcasite to ferric oxide.<sup>6</sup> In this case, the sulfur goes off in the form of alkali sulfides and thio-sulfates. It is stated that oxygen is not necessary for this action to occur. From these examples, it may be seen that pyrites may undergo secondary changes while in the underground coal.

Besides the sulfur coming from the original vegetable matter and that coming from percolating waters, there is a third possible source. While the coal is still in the process of formation, detritus is very liable to be mixed mechanically with the coal. This may account for not only a large part of the ash of coal, but also for some of the inorganic sulfur.<sup>7</sup>

The second general method in use for coal constitution study is that of destructive distillation. Because of the commercial importance of coking processes and gas manufacture this method has been studied more thoroughly than any of the others, and yet it is the poorest from the standpoint of determining the real nature of the coal substance. It is now a well proven fact that all of the products of distillation of coal do not



come from the coal by simple distillation, but that every one of them is the result of the decomposition of more complex compounds. A discussion of the destructive distillation of coal must be limited in this case only to those facts which tend to throw light on the nature of the coal substance itself.

The products resulting from the destructive distillation of coal consist of gaseous, liquid, and solid volatile matter and a residue which is largely carbon mixed with the ash of the coal. Among the volatile products might be mentioned ammonia, carbon dioxide, hydrogen sulfid, hydrogen, methane, carbon monoxide, nitrogen, acetylene, ethylene, various other hydrocarbons, pyridin, phenol, benzene, toluene, xylene, naphthalene, anthracene, phenanthrene, cresol and a great variety of other aromatic compounds. Because of the predominant presence of ring hydrocarbons and their derivatives, it has been supposed that the original coal consisted of ring like compounds.

H. Meyer<sup>s</sup> has an interesting theory concerning coal structure. He believes the main part of the coal to be composed of compounds which are very nearly polymers of acetylene, and break up very readily on heating into acetylene. The nitrogen exists in such a form that it will come out as either ammonia or hydrocyanic acid. When distilling the coal, these primary decomposition products unite in various combinations to give the ordinary distillation products. He performed some experiments to indicate this theory experimentally. By passing acetylene mixed in certain cases with ammonia or hydrocyanic acid through a heated tube, he obtained a variety of products, among which might be mentioned benzene, toluene, diphenyl, styrol, inden,





7  
naphthalene, anthracene, phenanthrene, pyrene, fluorene, acenaph-  
ten, chrysene, hexylene, pyridin, anilin, carbazol and benzonit-  
rile. All of these products, with the exception of the hexylene  
have been separated from coal tar. This theory of coal structure  
is at least partially correct, without much doubt, but as to  
whether it would apply to all the organic structure of the coal  
it would be impossible to state with the evidence at hand.

The largest part of the sulfur of coal comes off on dis-  
tillation as hydrogen sulfid<sup>e</sup>; but we also find thiophen compounds  
in the tarry distillate. The presence of hydrogen sulfide indi-  
cates not only the sulfur lost by the pyrites on heating, but  
may show the presence in the coal of complex organic sulfur com-  
pounds of a protein nature. From the theory of R. Meyer, we  
could expect the thiophen ring compounds to be formed by a sec-  
ondary reaction between acetylene and hydrogen sulfid. Therefore  
the presence of thiophen or its derivatives could hardly be con-  
sidered as proof of the existence in the coal of cyclic organic  
sulfur compounds.

The third method of attempting to determine the consti-  
tution of coal is by means of selective solvents. This is by  
far the best of the three, since any constituent obtained is  
either in the condition in which it existed in the coal or else  
the extraction reaction is of such a simple nature that the orig-  
inal substance can be easily deduced. This method of attacking  
the coal structure has been very little used for some time, but  
is now gaining a good deal of attention.<sup>9</sup>

The fact has already been mentioned concerning the solu-  
bility of the humus acids of peat in alkalies. This has led





F. G. Kaufmann<sup>10</sup> to regard peat as a mixture of two substances, dopplerite, the portion soluble in caustic alkali solutions<sup>11</sup> and another substance consisting of partly decomposed vegetable matter.

By the solvent method, peat has also been found to contain resinous substances running as high as 3.26 per cent of the content of the peat. The resins are extracted by using hot ether or alcohol as solvents.<sup>12</sup> They are rather important in this connection, since reference will be made to the resinous substances in coal later on.

In the lignites, resinoids and fossil hydrocarbons are abundant. The fossil hydrocarbons are generally visible as definite masses; the resinoids are very often disseminated throughout the coal, and here again we must have resource to solvent action. Benzene and other organic solvents will extract the resins, which have been found to be indefinite in composition. Watson Smith<sup>13</sup> states that he obtained 9.5 per cent of extractive matter by the action of benzene on a Japanese lignite.

Humus compounds are present in lignites, but not to such a great extent as in peat. We find, therefore, that xyloid lignite will dissolve in caustic alkali to a somewhat less extent than peat, and that very little solvent action can be obtained with the more compact lignites.<sup>14</sup> Bituminous and anthracite coals are not dissolved at all by alkaline solutions, so there must be a gradual destruction of the humus compounds during the coal evolution process. At times humus bodies are found in rather large percentages. Among the "paper coals" of Russia are found deposits of humic matter soluble in ammonia.<sup>15</sup> In Bohemian brown coal



von John found a humus acid soluble in ammonia or sodium carbonate with the approximate formula  $C_{46} H_{46} O_{25}$ .<sup>16</sup> A fossil humus from a Tertiary deposit near Cassel, Germany, furnishes the pigment known as Cassel brown.

Fremy<sup>17</sup> states that lignites are soluble in alkaline hypochlorites, while the older coals are not. Nitric acid attacks lignites very vigorously forming a yellow resinous body, which will dissolve in excess of the nitric acid or in alkaline solution.

This last property of the lignites is very important from the standpoint of coal constitution and has been used with marked success in the present research to determine several points. This treatment of coal with nitric acid can not be regarded as a simple solution method, yet it is included under this topic, because of the close analogy existing between the two.

E. Guignet<sup>18</sup> was the first investigator to study in much detail the action of nitric acid upon coal, and he concluded that the products formed were somewhat similar to the nitrocelluloses. This work was followed by that of R. J. Friswell<sup>19</sup>. Friswell fails to acknowledge the previous work of Guignet on this subject, but at the same time describes the phenomenon very accurately.

"If bituminous coal in fine powder be covered with rather more than double its weight of 49 per cent nitric acid, the mass rapidly becomes warm, and dense red fumes are given off. If 90 grams of coal and 200 c.c. of the acid are taken, the action is extremely brisk, and the frothing so violent that a 2000 c.c. flask is requisite to contain the mass. In about 30 minutes the action slackens, and heat being now applied, the action is kept





going at such a rate that a brisk evolution of gas continues; the solution is gradually raised to the boiling point and there maintained, the total time occupied being about six hours. The whole is now diluted, poured into a filter, and well washed. The filtrate consists of dilute nitric acid, with salts of calcium, iron, etc., in solution. The black residue on the filter is apparently unchanged coal. When washed free from acid, the residue is introduced into a flask and boiled with a dilute solution of sodium carbonate: nearly the whole dissolves, carbonic anhydride being briskly evolved. The resulting deep black-brown coloured liquid filters with great difficulty, but by careful treatment with water in deep vessels the insoluble matter from the 90 grams of coal was found to be 12.5 grams, consisting of coarse particles of coal, sand, etc."

He further goes on to say that with some coals, practically all of the organic matter of the coal could be taken into solution by this means, particularly if the coal were very finely divided. If the filtered solution be acidified with hydrochloric acid, a "bulky, deep brown-black, flocculent precipitate" is formed, which is insoluble in water containing traces of mineral salts or acids, but is fairly soluble in boiling distilled water, from which it separates again on cooling.

This "coal acid," as it is sometimes called, when dried at 100° forms shining black masses with conchoidal fracture. When heated on platinum foil, the substance swells up into a brilliant black mass, in this respect very much resembling a nitro compound of high carbon ratio. To test this out, Friswell attempted reduction by means of zinc dust and caustic soda and





also by sodium amalgam and acid reducing mixtures, but in no case was there formed a nitro reduction product. Dry distillation with zinc dust drove off the nitrogen in the form of ammonia, pyridin, and cyanides.

The coal acid seemed to be similar to the humus acids of peat, but different in several particulars. In the first place the coal acid is not hygroscopic as humus acids have been found to be; on drying the coal acid, it may again be dissolved, which is not true of humic acid; furthermore, the coal acid does not yield acetic acid on dry distillation. Some of the humus acids yield ammonia when boiled with alkalies, but the coal acid will not, which could be expected when it is considered that the evidence points very strongly to its being a nitro compound.

This work was followed up by that of Anderson and Roberts,<sup>20</sup> who investigated more particularly the ultimate composition of the coal acid, and its relationship to the type of coal. They found that the substance consisted of carbon, hydrogen, oxygen, nitrogen and sulfur with a small quantity of ash, mostly iron oxide. For the same type of coal they found the composition almost constant. On treating the coal with nitric acid and then with ammonia, only a very slight residue was left, which was found to consist of 36 per cent of mineral matter and occluded organic matter which was very similar to the coal acid, and which would probably have gone into solution had it not been so intimately mixed with the other residual substances. They assert that the presence of sulfur in the coal acid is the first proof of the existence of organic sulfur in the coal.

In order to get some more data on the nature of the coal



acid, Anderson and Roberts heated samples of Ell coal for four hours in a stream of carbon dioxide at 300°-315°C. At the end of this time the dry Ell coal was found to have lost about 9.5 per cent of its weight. The residue was treated in the usual manner to obtain the coal acid, and an ultimate analysis of this was then made. On comparing the analysis of this substance with that of the coal acid from the original coal, the two were found to be practically identical in ultimate composition. From this they draw the conclusion that the "nitrogenous molecule" of the coal is stable at that temperature. Other experiments, and particularly portions of the present research show that this organic component, comprising the larger part of the coal matter, is unusually stable, not only to heat but to many strong chemical reagents.

More work was done on coal solvents by a committee of the British Association,<sup>21</sup> but this work was largely incomplete. In addition to other solvents, they tried the action of a mixture of hydrochloric acid and potassium chlorate on coals. This oxidizing reagent seemed to differ in its mode of action from nitric acid in that the final product appeared to be a chlorinated substance.

A large amount of investigation has been undertaken by E. Donath on the reaction of nitric acid with coal.<sup>22</sup> He finds that dilute nitric acid will react vigorously with lignite, but has no action on bituminous coal, and concludes that the one is not a transformation product of the other, but have entirely different origins. This conclusion, although partially true, is probably too sweeping in character<sup>23</sup>.





Franz Fisher in recent years has tested the action of ozone on coal.<sup>24</sup> He finds that after ozone has been allowed to act on finely powdered coal, the coal is in such a condition that as much as 92 per cent of it may be soluble in water. The substance appears to be acidic in character, and is probably very closely related to the product resulting from the action of nitric acid on coal.

The solution methods so far given have been more particularly of a destructive nature to the coal substance. Other investigations have been carried on with simple solvents, which have presumably extracted the unchanged coal constituents.

In a report to the Commissioners of the 1851 Exhibition we find the first reference to work of this kind by Dr. Smythe of Göttingen. He tried the following solvents, given in the order of their extractive ability, on a brown Cologne coal, -- benzene, chloroform, alcohol, ethyl ether, petroleum ether, and acetone.<sup>25</sup>

Reinsch<sup>26</sup> in 1885 tried the action of alkaline solutions on the raw coals. Some mention of work of this kind has been made earlier: Reinsch believed coals to be composed of two characteristic substances, which could be distinguished by this reaction.

In 1901, Baker investigated the action of pyridin on coals.<sup>27</sup> He found that only a very small percentage of the anthracite coal was soluble, while in some cases as much as 20.4 per cent of bituminous coals went into solution. The solutions were brown colored and sometimes fluorescent. No relationship could be obtained in the proportion of the elements in the coal,





the residue and the extract. Anderson and Henderson also did some work on the pyridin solution of coal.<sup>28</sup> This investigation was undertaken with three types of coal, Japan, Bengal and Scotch, and the extracts from all seemed to be similar in properties and chemical constitution.

A similar research was carried out by Donath on a German coal.<sup>29</sup> By treating a coal with pyridin, he obtained a brownish-red solution, which gave a flocculent brown precipitate on addition of water or petroleum ether.

Bedson in 1908 performed quite a number of experiments with the pyridin extraction of coal.<sup>30</sup> He found that gas coals yielding 64-66 per cent of coke gave pyridin soluble material to the extent of 24-35 per cent. Bedson thought that the pyridin soluble substances had some relationship to the volatile matter, but this seemed to be disputed by the work of Dennstedt, Hassler and Bänz,<sup>31</sup> who found that coals yielding 62-87 per cent of coke (on an ash free basis) gave a pyridin extract of only 0.6-18 per cent of soluble matter. Wornast tried out the relationships on different gas coals.<sup>32</sup> A Lothringer gas coal yielding 50 per cent coke gave an extract of 12 per cent, while a Westphalian gas coal yielding 62 per cent coke gave 29 per cent. Rau concludes from results of this sort that in general more recent coals give a smaller extract than gas coals; that the maximum extract is reached at about a coke yield of 65 per cent; and that the amount of extract again decreases until anthracite coals give almost nothing.

Lewes investigated the action of pyridin on coal, particularly with reference to its effect on the coking properties.<sup>33</sup>



He states that the coking power of a coal is either mostly or entirely removed by the pyridin extraction, and ascribes this to the removal of resinic bodies necessary to the coking of a coal. The retention of the coking properties by some coals even after pyridin extraction he explains by assuming the presence of a resinic body not soluble in the pyridin. Lewes, in addition to previous investigators, had noticed that some coals yielded a higher percentage of volatile matter after extraction than before, and he believed that this phenomenon was due to the retention of some of the pyridin. His conclusions on the nature of the resinic bodies were that they were of two kinds, "the one easily oxidizable, soluble in pyridin and saponifiable by alkalies, and which on weathering is oxidized into a humus body with the evolution of water and carbon dioxide, and is responsible for the heating of coal in storage; the other class non-oxidizable, not saponified by alkalies, and forming with pyridin a compound insoluble in excess of the reagent, and this class may be the hydrocarbons from decomposed resins, as the residue in which they are present yields rich liquid hydrocarbons, as tar and pitch, but not rich in gas."

Wahl in 1912 investigated certain coals as to their action toward pyridin.<sup>34</sup> He found the volatile matter in the coal higher than that of the residue after pyridin extraction. The coke produced from the residue was more compact than that of the original coal.

In 1912, Frazer and Hoffman published the results of their researches on the action of phenol on coal.<sup>35</sup> Before deciding on the use of phenol as an extractive agent, various other sol-





vents were tried, but the three found to give the best results were phenol, pyridin, and anilin. A non-coking bituminous coal from Franklin County, Illinois was selected for the investigation. A large quantity of this was finely ground and extracted with phenol at 140 degrees C. for about 10 hours, after which the mixture was filtered. The extract was a dark red in color and was concentrated under diminished pressure to separate most of the phenol and then the remainder of the phenol was washed out by means of sodium hydroxide. The residue from the phenol extraction was not studied any farther, but the phenol soluble material was treated with a 10 per cent sodium hydroxide solution. Both the soluble and insoluble portions of this sodium hydroxide treatment were extracted with ether. In both cases, the ether insoluble compounds showed not only carbon, hydrogen and oxygen, but also sulfur and nitrogen as being present, while the ether soluble compounds showed only the first three. Each of the four mixtures were further separated by means of other solvents and fractional distillation in certain cases, until something like 30 different substances had been obtained and analyzed. Frazer and Hoffman assumed these substances to be the same as they existed in the coal, and thought that the evidence was fairly conclusive that they very nearly approached pure compounds.

In 1913, Pictet and Ramseyer extracted coal with benzene. The oil so obtained was fractionated by distillation and the different fractions studied. From this investigation, they believe coal to contain polymerized hydroaromatic hydrocarbons.<sup>36</sup>

From their work on the phenol extraction of coal in 1913, Clark and Wheeler believed coal to be composed of two types of





substances.<sup>37</sup> They called these the "hydrogen yielding" and the<sup>17</sup> paraffin yielding respectively. The distinction refers more to the ease of decomposition, since it has been found that there is a large amount of hydrogen given off between 750 and 800 degrees. They considered the pyridin insoluble substance to be a degradation product of cellulose. As to whether the pyridin extract consisted entirely of resinous material, they were somewhat doubtful, but when this pyridin soluble substance was extracted with chloroform, they were practically certain that almost pure resinous material was dissolved.

This work of Clark and Wheeler as well as that of White<sup>38</sup> and Jeffrey<sup>39</sup> have pretty definitely established the hypothesis of the two general types of bodies in coal, (1) the degradation products of cellulose, and (2), the resinic type of bodies.

In conformity with this idea, Parr and Hadley studied the phenol extraction of coal, with particular reference to the properties of both the extract and the insoluble residue.<sup>40</sup> The temperature in all of these experiments was above 110 degrees. The results of this work may briefly be summarized as follows. The amount of soluble material varied in different types of coal, for example, Vermilion County coals yielded 35-40 per cent of soluble matter; Madison and Montgomery County coals gave 30-35 per cent; and Williamson County coals only 20-30 per cent. All of these figures are on an ash and moisture free basis. The residue from the extraction would not coke, which showed that the coking constituent was in the phenol extract. Both residue and extracted material oxidized at room temperature and more rapidly at 100 degrees. The extract con-



tained more volatile matter than the residue, although the ultimate composition was about the same in both cases, and the gases given off have about the same composition, also. Some other facts concerning the oxidation of coal were brought to light by this process.

The method of extraction which Parr and Hadley used was continuous in its action, that is, fresh solvent was at all times acting on the finely powdered coal. The coal was contained in an extraction thimble supported in a Kjeldahal flask, in the bottom of which was the boiling phenol. The vaporized phenol was condensed at the top of the flask by a boiling toluene condenser, so that the phenol would drop on the coal at a temperature of 110 degrees or more. Carbon dioxide was passed through the extraction flask to prevent oxidation by the air.

As regards the distribution of sulfur between the residue and extract, the following statement is made.

"It is to be noted that the percentage of sulfur in the residue is high. This is to be accounted for by the fact that the residue contained practically all of the ash that was present in the coal. That there was some sulfur in the extract was taken to indicate that a part of the sulfur in the coal was present in the organic form."







### Conclusions

Despite the thorough character of some of the researches briefly abstracted above, very little of a definite nature has yet been brought to light concerning the constitution of coal. A few of the general deductions may be summarized here.

1. Coal consists of carbon, hydrogen, oxygen, nitrogen and sulfur, together with a varying amount of mineral ash.

2. The combinations of these five elements between each other are unknown, except that some of the hydrogen and oxygen are combined as water, and in some cases, as in mother coal, amounts of charcoal or free carbon have been found. The presence of any considerable amount of free carbon in the coal texture is doubtful, except perhaps in the extreme anthracites.

3. There seem to be two types of bodies in the organic structure of the coal, (1) degradation products of cellulose, (2) resinic bodies. The first type exists in lignites and other recent coals as bodies distinctly related to the humus acids and soluble in alkalis; in the true coals this relationship ceases to exist, but bodies similar to these are produced by various oxidizing agents. The second type of bodies are found in a condition closely resembling resinic bodies of vegetable matter and have probably not been changed much during the coalification process. They may be extracted from the coal by means of organic solvents, particularly phenol, pyridin, and anilin.

4. Some evidence seems to point to the presence of hydrocarbons in the coal. Because of the large number of aromatic compounds found in the distillate, the coal may contain polymers



of acetylene or closely related substances.

5. The organic sulfur and nitrogen of the coal probably exist in a form similar to that of protein sulfur and nitrogen. This seems to be indicated by the origin of coal and also by the nature of the distillation products.

6. The mineral or inorganic portion of the coal is generally present in comparatively small quantities and consists of iron pyrites (or marcasite), calcium carbonate, and silicates of various kinds, in addition to other substances peculiar to certain coals.





## The Development of a Method for Analysing the Different Forms of Sulfur in Coal.

Introduction and Historical. Many methods have been devised for the determination of the total sulfur in coal, all of them depending on the use of an oxidizing reaction sufficiently strong to convert every form of sulfur in the coal into soluble sulfate. The practical importance of total sulfur determinations has long been recognized because in the combustion of high sulfur coals large quantities of corrosive gases are given off, and also in coking processes a large percentage of the sulfur is retained in the coke.

However, any relationship between the amount of total sulfur and the amount of sulfur in flue gases or coke has never been found. The main reason for this is that the sulfur does not exist in one form only, but in several entirely different combinations, and any method for analysing the separate forms of sulfur in coal would go a long way toward solving these problems. Engineers are now realizing the importance of such a method, since data obtained from such analyses would give information necessary in deriving the correct heating value of the coal, the amount and character of corrosive gases, and the distribution of sulfur in coking, while a total sulfur analysis gives this data in only a very general manner.<sup>41</sup> The scientific value of some method for accomplishing this is of equal importance, since it would be one more step toward the determination of coal constitution.



W. A. Bradbury in 1878 indicated that sulfur exists in coal in organic combination.<sup>42</sup> The first method proposed to determine this organic sulfur separately from the inorganic was that of T. M. Drown.<sup>43</sup> He treated the finely powdered coal with a sodium hydroxide solution of 1.25 sp. gr., which had previously been saturated with bromine. After this sodium hypobromite treatment, the solution was acidified with hydrochloric acid, and then, if necessary, the hypobromite treatment repeated on the residue. The solution was evaporated to get rid of silica, taken up in hydrochloric acid and water, and the sulfate precipitated. Drown claims that only the sulfur existing as pyrites and sulfate are taken into solution by this method, thereby leaving the organic sulfur in the residue.

The same investigator also tried the effect of hydrochloric acid and potassium chlorate on the same coals. By this method, the coals having a small percentage of pyrites gave the same results as with the other method, but those containing much pyrites gave higher results. With the hypobromite method very good checks were obtained, but as to whether only the inorganic sulfur was being dissolved, the author could offer no proof.

The next year Helm attacked the problem from the side of the organic sulfur constituents.<sup>44</sup> He tried the action on coal of alcohol, ether, benzene and alcoholic potassium hydroxide with the idea of extracting all of the organic sulfur. Nothing definite, however, resulted from this work.

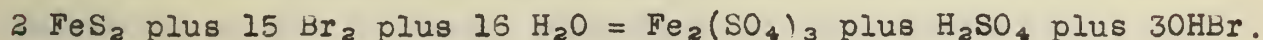
Ferd. Fisher followed up the work of Drown on the separation of the inorganic from the organic sulfur.<sup>45</sup> He treated samples of powdered coal with water and then added bromine grad-





ually. At the end of five hours the reaction was complete, but if the water had been heated to 70 degrees before beginning, the time required was only one half hour. The mixture was filtered and sulfur and iron determined in the filtrate.

Bromine reacts with pyrites as follows:



The pyrites should therefore all pass into solution, and both the iron and sulfur would be found in the filtrate. Fisher at this time recognized that iron existed in other forms than pyrites, since the residue from these extractions contained considerable iron. The ratios between the percentages of iron and sulfur in the filtrate were variable and did not indicate that only the pyrite was being extracted. In some cases the sulfur was higher than indicated by the formula  $\text{Fe S}_2$ , while in others the sulfur was lower. This latter discrepancy was explained by assuming that another form of iron went into solution or that all of the sulfur had not been brought fully into solution. Apparently no dilute hydrochloric-acid-soluble-iron or sulfur had been determined on the coals worked with.

Fisher believed that the method used by him was unsafe as a means for determining the inorganic as distinguished from the organic sulfur, since some of the organic sulfur might be oxidized by the bromine to sulfate and on the other hand, some of the sulfate might be taken up by unsaturated organic compounds. From his investigations, Fisher came to the conclusion that the larger part of coal sulfur was in the organic form, a fact which had not received much consideration up to that time.

In more recent years a method has been used for the



determination of the different forms of sulfur in coal depending on certain assumptions regarding the structure of coal. In the first place, all of the iron not soluble in dilute hydrochloric acid is assumed to be combined as pyrites, and the pyrite sulfur is therefore figured out on the basis of  $\text{Fe S}_2$ . However, iron may exist as the silicate, sometimes in large quantities, so this makes a very weak point in this scheme of analysis. The sulfur soluble in dilute hydrochloric acid is taken as the sulfate sulfur, which is undoubtedly correct. After determining these two forms of sulfur, all the rest is figured as organic sulfur. No proof has as yet been given, however, that the remainder is entirely organic sulfur. Because of the assumptions on which this method depends, and the indirect manner of arriving at results, some effort has been made to get a more exact and direct procedure.

In 1915, Mr. E. E. Charlton performed some experiments in this laboratory looking toward a direct method for the determination of organic sulfur in coal. His process was essentially the phenol extraction method of Parr and Hadley previously described. The residue and extract were therefore analysed for their sulfur content by sodium peroxide fusion. His procedure was based on the theory that the residue or insoluble portion of the coal left after the phenol treatment contained all of the inorganic sulfur and that the portion soluble in phenol contained all of the organic sulfur. This hypothesis seemed to apply in the case of low-sulfur coals but in high sulfur coals the amount of sulfur remaining in the insoluble residue was out of all proportion to the iron present making it impossible to assign such sulfur to any known mineral combination. Hence the question arose as to whether the phe-





nol was taking out all of the organic sulfur and that an unknown inorganic form still remained in the residue, or whether the phenol was indeed not extracting all of the organic sulfur. That the extracted sulfur compounds were organic was definitely proven by the fact that the soluble material left no ash on ignition.

It was with regard to this discrepancy, especially among the high sulfur coals, that the present research was undertaken. Not only was the phenol extraction method to be tried out with the idea of arriving at some explanation for the observed differences, but if necessary a new method of analysis devised.



## Experimental

### Method Involving the Use of Organic Solvents

As stated before, the first method used for attacking the problem was that of organic solvents for removing the organic compounds. The general procedure for trying this out was as follows:

A sample of coal was obtained, together with any information as to where and how recently it had been mined, and any other facts pertinent to the investigation. No effort was made to get representative samples, since a study of the sulfur compounds in one piece of coal would give similar results to an examination of a mixed sample, as far as the general structure of the coal and a method of analysis were concerned. This sample was then ground to about the size of a pea by a rotary crusher, and the coarsely divided coal was spread out in a thin layer for several hours so as to get the sample as near to ordinary room moisture conditions as possible. It was then ground to 100 mesh size by means of a buck board and muller, and stored either in a rubber stoppered Erlenmeyer flask or a clamp lid Mason jar.

As a means of comparison, the method decided upon for arriving at the percentage of the different forms of sulfur was as follows. A total sulfur and a total iron determination were made on a small quantity of the sample, and also a determination of the sulfur and the iron which were soluble in dilute hydrochloric acid on a larger amount. The percentage of total iron minus the percentage of hydrochloric-acid-soluble iron was con-





sidered to be the percentage of pyritic iron in the sample. The pyritic sulfur was figured from this, assuming the pyrites always to have the formula  $\text{Fe S}_2$ . The sulfate sulfur was that obtained in the hydrochloric acid extract, and the organic sulfur was taken as the difference between the total sulfur and the sum of the two inorganic forms. This method for determining the different sulfur forms has had no exact experimental confirmation, but was the best available at the time.

The amount of sulfur containing compounds which were capable of extraction by various organic solvents on the coal was then subjected to investigation, and the results of the two methods compared to find if possible any relationship between the percentage of soluble sulfur and that of the organic sulfur determined as above. The solvent with which the greatest amount of work was done was phenol. In a few cases, the amount of sulfur in the phenol extract was determined, but since this was both a difficult and an inaccurate procedure, in all cases the residue was analysed for its sulfur content, and the difference between this and the total sulfur was considered to be the sulfur in the extract. Throughout the investigation, the percentages of both iron and sulfur were always figured on the basis of the original coal weighed out. It was only by following this plan that comparative results could be obtained.

The first method used in this investigation to analyse for the total sulfur and iron in the coal was that of Eschka and Fresenius. Although this gave fairly good results for the sulfur, the iron was generally too low. A sodium peroxide fusion method was then substituted for this which gave excellent results, and



this procedure was followed for the analysis not only of the coal, but also for sulfur and iron in all residues of every description during the investigation.

This fusion was carried out in a pure nickel crucible of about 50 c.c. capacity and having a rather loose fitting lid. Some sodium peroxide was placed in the bottom, and on top of this the substance to be analysed in a finely powdered condition. The crucible was then filled about half full with sodium peroxide, the amount depending on the quantity of coal substance added. With coal itself, half gram samples were used. The contents were thoroughly mixed by means of a glass stirring rod, and a thin layer of sodium peroxide sprinkled over the top. The lid was put in position, a piece of metal weighing a few ounces placed on it, and the charge ignited by heating the outside of the crucible by means of a Bunsen burner. Almost without exception, complete combustion of the organic matter occurred in a few seconds, without any of the charge blowing out under the lid. The crucible was cooled somewhat, and then the fusion was dissolved out with water. The alkaline solution was carefully acidified with hydrochloric acid and filtered.

From this point in the analysis there was little variation from the ordinary methods of determining iron and sulfur in a solution. The hot solution was poured into a slight excess of ammonia and the mixture stirred to coagulate the ferric hydroxide. This was filtered off, dissolved from the filter by concentrated hydrochloric acid, and the amount of iron was determined by the usual Zimmermann-Reinhardt procedure. Since the quantities of iron dealt with were small in nearly all cases, the potassium







permanganate solution used was weaker than ordinary, it having a strength about one-fortieth normal.

The filtrate from the ferric hydroxide was made slightly acid with hydrochloric acid, brought to boiling, and 10 c.c. of 10 per cent barium chloride added slowly. The solution was heated and stirred for some time, since it was particularly important that none of the barium sulfate should pass through the filter, as the amount of precipitate was small, and a slight loss would have caused quite a considerable percentage error. After filtering, the filter was ignited in a porcelain crucible and the barium sulfate weighed.

It will be noticed that the method outlined above varies in two particulars from that ordinarily used. No oxidizing agent is added before precipitating the iron or the sulfur, since the sodium peroxide fusion has accomplished that end. Furthermore, the second precipitation of the iron to remove any basic sulfate is omitted, because the amount of precipitate is so small compared to the volume of the solution. In order to show that this second precipitation was unnecessary and that the method used was accurate enough for the purposes of the investigation, the following experiment was performed.

Two samples of pure ferrous ammonium sulfate were weighed out, one corresponding roughly to the sulfur content of one gram of a low sulfur coal, the other to that of a very high sulfur coal. The samples were dissolved in very dilute hydrochloric acid, oxidized by boiling with bromine water, and then run through the analysis just described.



Table No. 1

## Check Analysis of Ferrous Ammonium Sulfate.

Weight of sample	.0729 g.	.3080 g.
Theoretical per cent iron	14.3	14.3
Per cent iron determined	14.4	14.2
Theoretical per cent sulfur	16.4	16.4
Per cent sulfur determined	16.5	16.3

If larger samples had been used, the error would probably have been still smaller. However, for the size of samples of coal used in this work, the corresponding error will not be greater than .01 per cent. As no conclusions are drawn within this amount, the method is amply suited to the conditions of the work.

The determination of the sulfur and iron of coal soluble in dilute hydrochloric acid was carried out as follows. Samples of the coal weighing five grams were treated with 300 c.c. of 3 per cent hydrochloric acid. This was allowed to digest at 60 degrees C. for 40 hours. The solution containing the soluble iron and sulfate sulfur was filtered off, oxidized by means of bromine water, and analyses run for both the sulfur and iron exactly as in the sodium peroxide fusion method just described. This procedure is accurate as a means of extracting the sulfates, and none of the other sulfur forms are affected as shown by the fact that certain coals known to contain large quantities of pyritic and organic sulfur yielded no sulfur whatever with this extraction.

The methods just described would furnish the necessary





information as to the percentages of the different forms of sulfur in the coal, provided that the assumptions are correct. The next step would be the extraction of the coal with phenol and this was carried out in a somewhat different manner from that usually employed. Instead of using an extraction thimble, containing the coal with hot condensed phenol dropping onto it, a flask with both the finely powdered coal and the phenol in it was heated to 140 degrees C. by means of an electric oven. An Erlenmeyer flask of about 100 c.c. capacity was chosen, and in it was placed one half gram of the coal to be studied. On it was poured 25 c.c. of molten phenol and in the neck of the flask was inserted an air condenser about two feet long. The flask was then placed in the inner chamber of the electric oven, with the condensing tube extending through the top, and heated at 140 degrees for twenty hours.

At the end of this time, the flask was removed and the contents promptly filtered through a Gooch crucible previously prepared. The flask was thoroughly rinsed with alcohol to remove any particles of residue and also to dissolve out the excess phenol from the residue in the crucible. This was followed by an ether washing, and the residue was then allowed to dry in the Gooch crucible.

As was mentioned before, in a few cases the phenol extract was analysed for its sulfur content, but this made a difficult and inaccurate procedure. When this was done, the dark red extract was evaporated in a porcelain dish heated by the electric oven. When almost all of the phenol had been driven off, the dish was allowed to cool and the substance left carefully scraped out by means of a spatula. It was finely powdered and



fused with sodium peroxide in order to get the sulfur into solution for analysis. To prevent the oxidation of the extracted substance while in the oven, a slow stream of carbon dioxide was passed through the heating chamber.

The most accurate and most convenient way of arriving at both the residual and the extracted sulfur is the analysis of the phenol residue, however. This was accomplished by removing the asbestos mat and all of the residue from the Gooch crucible and mixing it up thoroughly with sodium peroxide. From this point the analysis was the same as that for the total sulfur in coal. Care had to be taken to make the asbestos mat as thin as possible, since the subsequent fusion with sodium peroxide took most of the asbestos into solution and then trouble might be encountered later with the silicic acid when the barium sulfate was precipitated. With this precaution observed, however, the solution did not need to be evaporated to remove the silicic acid, since this does not precipitate with barium in dilute solutions.<sup>46</sup> The difference between this residual sulfur as determined and the total sulfur must be the sulfur extracted by the phenol.



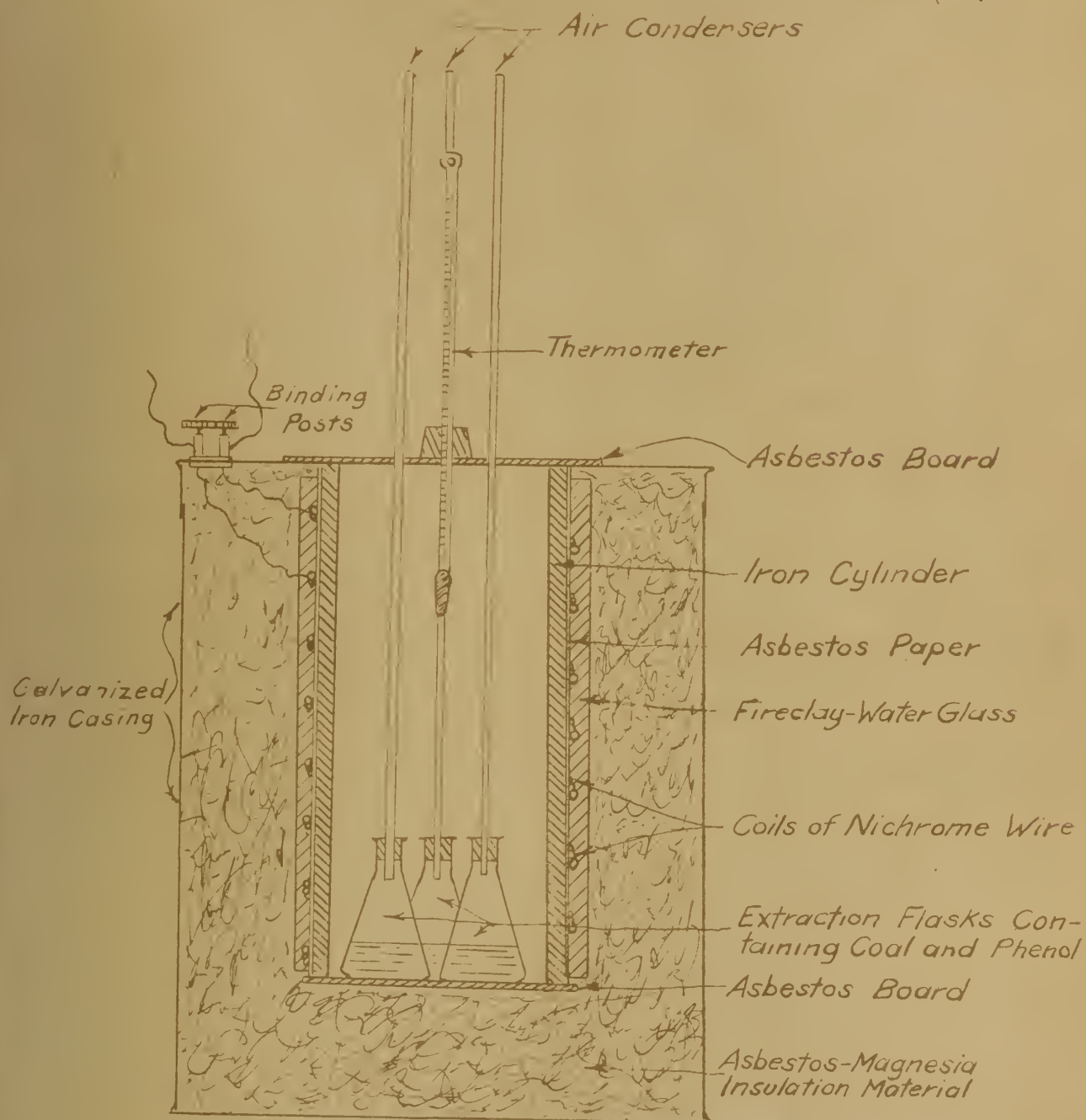


### Description of Apparatus

The electric oven used in the work was constructed especially for the phenol solution experiments. The cylindrical casing was made of galvanized iron and was 14 inches high and 12 inches in diameter. The inner chamber was a cylinder of heavy iron, 10 inches high and 5 inches in diameter. Around this was wrapped some asbestos paper and then "nichrome" resistance wire in the form of a coil. For this purpose, fifty feet of No. 20 wire was wrapped into a one-quarter inch coil, doubled at the middle and coiled around the cylinder ten times so that the two ends came out at the top. On top of this wire was put a one-half inch layer of fireclay-water glass mixture. The space between the inner chamber and the casing was filled with an asbestos-magnesia mixture. 110 volt alternating current was used, and with no other resistance than the wire of the oven, the current flowing was 3.1 amperes. However, in order to keep the temperature down to the 140 degrees desired, it was necessary to put some lamps as resistance in the circuit.

In the work done by Parr and Hadley on phenol extraction, an effort was made to exclude air from the extraction chamber by the use of a stream of carbon dioxide. The method used in this investigation did not require this precaution as shown by the following experiment. Two flasks were used, one of which had the air condenser open at the top as usual, and the other was closed as follows. The open end connected to a U tube containing alkaline pyrogallol and this to another U tube containing water. By means of a pump, the air was drawn out of the flask and was





## PLATE I

CROSS SECTION SHOWING  
ELECTRIC FURNACE  
USED IN PHENOL EXTRACTION OF COAL





then allowed to return through the two U tubes. Thus only nitrogen was in the extraction flask during the entire process. After the usual process had been followed through, the following results were obtained:

Total sulfur in coal	2.18%
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Residual sulfur with open condenser	2.03%
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Residual sulfur with nitrogen atmosphere	2.06%
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In several other cases the same test was applied and no essential difference was noticed. The open end condenser was therefore used in nearly all of the extraction work.



### Description of Coals

Ten different coals were studied during the investigation. A very brief description of each is given below.

Coal No. 1. A Vermilion County coal taken from an Illinois Traction Company car in October, 1915.

Coal No. 2. A Vermilion County coal obtained from a mine near Georgetown, May 19, 1915.

Coal No. 3. A Vermilion County coal collected from Kelly No. 4 mine at Westville, March, 1916.

Coal No. 4. A Vermilion County coal obtained from the Danville Colliery Company at Catlin, October 25, 1916.

Coal No. 5. A Saline County coal from near Harrisburg, April 1, 1915.

Coal No. 6. A Vermilion County coal from the Danville Electric, June 10, 1915.

Coal No. 7. A Vermilion County coal from the Danville Colliery Company at Catlin, February 3, 1917.

Coal No. 8. A Tennessee coal of the Jellico type known as "Black Beauty", obtained about May, 1917.

Coal No. 9. A Japanese coal containing large clumps of resinous material. Mined December 1913.

Coal No. 10. A Tennessee coal of the Jellico type obtained April 1, 1915.

Out of the ten coals used, seven were Illinois coals, one of these coming from Saline County and the other six from Vermilion County. The Vermilion County coals were the best suited to the work, since the sulfur content was nearly always high





and comparatively large amounts of the different sulfur forms were found. No work whatever was done on Eastern anthracites, since they contain so little sulfur.

All of these samples were powdered and put in air tight containers on the date mentioned and were studied at times varying from one day up to almost three years afterwards. Since the purpose of the investigation was to study the sulfur forms of coal, this variation in the age of the samples was advantageous rather than otherwise since a greater variety of data could be obtained. Particularly was this the case with regard to the sulfate sulfur which increases in most coals rather rapidly on standing, and for this reason the hydrochloric-acid-soluble iron and sulfur were re-determined before each set of data was taken on a coal.

The proximate analysis of each of these coals is given in the following table.

Table No. 2

Proximate Analyses of Coals (Per Cent)

No. of Coal	Moisture	Volatile Matter	Fixed Carbon	Ash
1	6.77	41.37	43.48	8.38
2	4.26	34.24	45.29	16.21
3	11.37	35.85	47.83	4.95
4	5.98	42.82	45.90	5.30
5	4.72	34.73	54.29	6.26
6	5.54	38.36	40.13	15.97
7	2.69	42.81	45.05	9.45
8	1.63	37.39	58.22	2.76
9	2.05	44.47	42.40	11.08
10	3.53	35.97	59.54	0.96



The analyses for sulfur and iron on each of the coals, calculated on an air dry basis, is given below. Unless otherwise stated, all percentages throughout the investigation are calculated back to the weight of the air dried coal used.

Table No. 3

## Sulfur and Iron Content of Coals (Per Cent)

No. of coal	Total Sulfur	Total Iron	HCL sol. Sulfur	HCL sol. Iron
1	2.68	1.36	0.04	0.14
2	2.18	1.65	0.17	0.27
3	0.64	0.21	0.00	0.06
4	2.14	0.69	0.05	0.07
5	1.20	0.55	0.25	0.20
6	5.00	3.40	1.31	1.62
7	3.31	1.87	0.01	0.07
8	1.02	0.82	0.01	0.12
9	1.40	0.95	0.02	0.29
10	0.94	0.38	0.02	0.11

In this table an effort has been made to give the percentage of hydrochloric-acid-soluble sulfur and iron at about the same time as the phenol extraction was made. As already mentioned these values change somewhat rapidly, so this determination was repeated at intervals during the progress of the investigation.





Results Obtained by Organic Solvent Methods.

The results of the phenol extraction of these coals is given in the next table, together with a comparison with the organic and inorganic forms of sulfur in the coal as calculated from the above data. The method used in calculating these has already been indicated, but it may well be repeated here in a somewhat more definite manner. The pyritic sulfur, that is, the sulfur combined as iron pyrites or marcasite, was deduced by subtracting the soluble iron from the total iron and then multiplying this by 1.145 which is the chemical factor for the conversion of iron into sulfur when they are combined as pyrite. The sulfate sulfur was considered the same as the soluble sulfur. The organic sulfur was obtained by subtracting the sum of the two inorganic forms from the total sulfur. In the last column is given the difference between the organic sulfur as figured by this method and the phenol extracted sulfur.



Table No. 4

## Sulfur Extracted by Phenol and Comparison with Organic

Sulfur (Per Cent)

Coal No.	Total Sulfur	Sulfur as Fe S <sub>2</sub>	Sulfur as Sulfate	Total Organic S by Difference	Organic S: Soluble in Phenol	Difference between Total Organic S and Phenol Soluble S
1	2.68	1.39	0.04	1.25	0.42	0.83
2	2.18	1.58	0.17	0.43	0.15	0.28
3	0.64	0.17	0.00	0.47	0.20	0.27
4	2.14	0.71	0.05	1.38	0.34	1.04
5	1.20	0.40	0.25	0.55	0.16	0.39
6	5.00	2.03	1.31	1.66	0.77	0.89
7	3.31	2.06	0.01	1.24	0.50	0.74
8	1.02	0.80	0.01	0.21	0.10	0.11
9	1.40	0.75	0.02	0.63	0.21	0.42
10	0.94	0.31	0.02	0.61	0.12	0.49





It can easily be seen from this table of experimental results that no relationship whatever exists between the amount of sulfur extracted by the phenol and the amount calculated by difference to be present as organic sulfur except that the latter is always considerably larger than the former. This may be due to any one of several conditions. In the first place, the phenol may not extract all of the organic sulfur compounds, or again, the sulfur may be present in some undetermined inorganic form. Also, the standard of comparison has not been definitely proven correct for the iron considered to be pyritic iron may be combined with more sulfur than the theoretical amount for pyrite; or it may be combined with less, which is the case to a certain extent if the coal contains iron silicate.

Whatever the cause, a wide gap exists between the total sulfur by difference and the sulfur whose character is known. That the phenol extracted sulfur is organic in nature can not be doubted since the extract is practically ashless, and the sulfate sulfur must be present as such. This leaves, then, two questions to be settled. First, is the iron, assumed to be combined as pyrites, quantitatively present as such? And, second, what is the nature of that sulfur assumed to be organic and not extracted by phenol, the quantity of which is probably represented for each coal in the last column of the above table?

This last mentioned problem was attacked first by the use of other solvent methods. Higher temperature or longer time of extraction by the phenol were not considered practicable in the light of former research on these points. That the method used in this investigation was equal to or better than the extraction



thimble process of Parr and Hadley and Charlton, as far as the amount of sulfur extracted was concerned, was shown by a comparison between the two methods on the same coals. In every case, the percentage of sulfur extracted by the phenol was slightly greater when determined by the method here described. Since no further help could be obtained from phenol extractions of coal, other solvents were sought for in extracting the coal sulfur compounds.

In addition to phenol, both pyridin and anilin have been used to quite an extent for determining the constitution of coal. Since no work had been done with regard to the amount of sulfur extracted by these solvents, some experiments of this nature would be essential in the investigation. For this purpose some of coal No. 1 was extracted with pyridin and another sample with anilin. From this qualitative test there appeared to be about as much sulfur in the extract as there was with phenol. Furthermore, these solvents resembled phenol in that they had no effect on iron pyrites and calcium sulfate.

In order to test this out quantitatively, 0.5 gram samples of coals Nos. 1 and 3 were extracted with 25 c.c. of anilin, using the same method of procedure as with phenol. The temperature of the extraction was 140 degrees. The results of this are given below.

Table No. 5

Coal No.	Sulfur Extracted by Anilin (Per Cent)			
	Total Organic S by difference	Organic S Soluble in Phenol	Organic S Soluble in Anilin	Difference between Total Organic S and Anilin soluble S
1	1.25	0.42	0.44	0.81
3	0.47	0.20	0.09	0.38





Comparing these results with those obtained by the phenol extraction, it may be seen that for coal No. 1 they are about the same and for coal No. 3 not even so good. Nothing can be deduced from this experiment, of course, as to whether the anilin soluble sulfur constituent are the same as the phenol soluble.

Another extraction experiment was tried in which a mixture of equal parts phenol and aniline acted as the solvent. The conditions for this determination were the same as above. The following result was obtained.

Table No. 6

## Sulfur Extracted by Phenol and Anilin (Per Cent)

Coal No.	Total Organic S by Difference	Organic S Soluble in Phenol	Organic S: Soluble in Phenol and Anilin	Difference between Total Organic S and Phenol-Anilin Soluble S.
1	1.25	0.42	0.53	0.72

This seemed to give somewhat better results, but the unaccounted-for sulfur was still so large that the method was not much better from a practical point of view. Theoretically, it was interesting, as it indicated that different constituents might be extracted by the basic anilin than those extracted by the acid-like phenol.

The extractions with pyridin had to be carried out at a lower temperature than those with phenol and anilin, because of the lower boiling point. The temperature chosen was 85 degrees. The results are given below.



Table No. 7

Coal No.	Sulfur Extracted by Pyridin (Per Cent)			
	Total Organic S by Difference	Organic S Soluble in Phenol	Organic S: Soluble in Pyridin	Difference between Total Organic S and Pyridin Soluble S
1	1.25	0.42	0.35	0.90
2	0.43	0.15	0.13	0.30

The sulfur extracted by pyridin is not so great as that taken out by phenol, so that there would be no advantage in using this as a solvent. The extractive power of benzene was also tried, but practically no sulfur whatever was detected in the filtrate. From the experimental data just given, it appeared to be a hopeless task to take out all of the organic sulfur by means of an organic solvent, so other solvents were sought to help accomplish this purpose.

#### Methods Involving the Use of Inorganic Solvents

The first one of these tried out was sodium hydroxide. 0.5 g. of the coal was extracted with phenol as usual, and then the residue was further treated with 50 c.c. of 5 per cent sodium hydroxide. This was allowed to stand at room temperature for 48 hours, filtered, and the filtrate oxidized by means of sodium peroxide. From coal No. 1, with unaccounted-for sulfur amounting to 0.83 per cent, there was obtained by this method 0.23 per cent; from coal No. 2, with unaccounted-for sulfur 0.28 per cent, the sodium hydroxide extracted 0.39 per cent. Evidently all of the organic sulfur is not extracted by the sodium hydroxide in some





cases, and a good deal of doubt could exist as to whether all of that extracted is organic.

Another inorganic solvent tried out was potassium permanganate. Qualitative tests showed this to have quite a solvent action on iron pyrites. On coal it also reacted rather quickly and took into solution a quantity of sulfur. In both cases, the permanganate decolorized quickly and large quantities of manganese dioxide were precipitated. In no case, however, did the sulfur extracted by the permanganate approach the pyritic sulfur in amount. This seemed to be due to the fact that the coal substance proper reacted so readily with the permanganate that repeated treatments were necessary to insure complete oxidation of the pyrites. Although the potassium permanganate oxidized the pyrites, it was rather doubtful whether it would take into solution the sulfur of the coal as yet unaccounted for. Because of the discordant and inconclusive results obtained and the large quantities of manganese dioxide precipitated, this method of attack was abandoned.

The next solvent tried was concentrated nitric acid. This was known to be a complete solvent for the pyrites, but as to whether it attacked and took into solution the stabler organic sulfur compounds of the coal was still to be determined. Gram samples of the coals were placed in beakers and covered with 25 c.c. of concentrated nitric acid. After 24 hours extraction, the following percentages of sulfur were found in the filtrate. Under each percentage is given the corresponding per cent of combined sulfate and pyritic sulfur.



Table No. 8

## Concentrated Nitric Acid Extraction of Coal (Per Cent)

	Coal No. 1	Coal No. 2	Coal No. 4
Sulfur in $\text{HNO}_3$ Extract	1.20	1.47	0.41
Pyritic and Sulfate Sulfur	1.43	1.75	0.76

These results are apparently not in accord with theory in that the nitric acid does not seem to be extracting quite all of the pyritic and sulfate sulfur, and perhaps this is true to a certain extent since the extraction was carried out at room temperature. But here again, the assumption on which the pyritic sulfur is figured is indicated as not being true, since some of the iron assumed to be pyritic is probably silicate iron and therefore the pyritic sulfur is high. However, the main object of this experiment, which was to find out if any of the organic sulfur was oxidized and taken into solution, seems to give a negative result. At least, the figures above would indicate that scarcely any of the organic sulfur was affected.

All of the experiments performed up to this point would tend to show that the unaccounted-for sulfur was combined in an extremely stable form. The failure to respond to the nitric acid treatment, especially, would indicate this. However, there might be a possibility of free sulfur being left in the residue after extraction with nitric acid. In order to find this out, the nitric acid treatment above described was repeated, and then the residue was boiled with pure carbon tetrachloride to remove any free sulfur that might be there. The carbon tetrachloride was evaporated off, and the slight residue mixed with benzoic acid





and fused with sodium peroxide. This fusion was added to the nitric acid extract and the sulfur was then determined. By this modified method, the sulfur in the extract of coal No. 1 was raised 0.02 per cent and that of coal No. 2, 0.08 per cent. It would therefore appear that the formation of free sulfur during the nitric acid treatment is of minor importance.

The only common inorganic substances which might conform to the conditions as thus given are certain sulfides and a few insoluble sulfates. On making a sodium peroxide fusion of coal No. 4, acidifying with hydrochloric acid and passing in hydrogen sulfide, no precipitate other than a little free sulfur was obtained, thereby definitely proving the absence of arsenic or any other metal which might make an insoluble sulfide. An excess of sulfuric acid was added to another portion of sodium peroxide fusion solution, but no precipitate was observed, and this showed the absence of metals forming insoluble sulfates. Thus, by a process of elimination, the unknown sulfur of the coal was almost certainly reduced to some organic form. That this is so is proven by certain experiments which will be described later.

Although the concentrated nitric acid had proven a failure as far as the stable organic sulfur was concerned, it proved to be almost an ideal solvent for the two inorganic forms, namely, the sulfate sulfur and the pyrites. The data given in the last table seemed to indicate that not all of the pyritic sulfur was being extracted by the concentrated nitric acid. That all of the pyrites was extracted, and that the difference was due to false assumptions in the calculation of the pyritic sulfur will be shown later.



The method used in treating the coals with the concentrated acid was very simple. 25 c.c. of concentrated nitric acid was poured over one gram of the coal and the mixture was allowed to stand 24 hours before filtration and analysis of the extract. The results are given in the following table, together with the percentage of the combined pyritic and sulfate sulfur as figured by the old indirect method and the total iron in the coal.

Table No. 9

## Concentrated Nitric Acid Extraction of Coal. (Per Cent)

Coal No.	Sulfur in Acid Extract	Iron in Acid Extract	Pyritic Sulfur (as calculated from supposedly Pyritic Iron*) plus Sulfate Sulfur in Coal	Total Iron in Coal
7	1.72	1.53	2.07	1.87
7	1.76	1.52	2.07	1.87
7	1.77	1.51	2.07	1.87
7	1.72		2.07	
7	1.77		2.07	
7	1.69		2.07	
4	0.65	0.62	0.76	0.69
4	0.65	0.58	0.76	0.69

\*Pyritic Iron = Total Iron minus H Cl Soluble Iron

If the old method for calculating the pyritic sulfur were correct, the two iron values should correspond and also the two sulfur values, or else the nitric acid extract sulfur percentage should be a little higher due to partial oxidation of the organic sulfur. On the other hand, the calculated values are all high as compared with those obtained directly.





Some doubt was felt at this point in the investigation as to whether or not all of the pyrites were being taken into solution by the nitric acid, and a set of experiments was started to find out the effect of aqua regia on the coal. The method of procedure was much the same as with the nitric acid, except heat was used to hasten the solution process, thereby reducing the time to about one hour. The solvent used consisted of one part of concentrated hydrochloric acid to three parts of concentrated nitric acid. Whereas but 0.65 per cent of sulfur had been extracted from coal No. 4 by means of nitric acid, the hydrochloric-nitric acid treatment yielded 0.74 per cent in a very short time, and 0.90 per cent during several hours on the water bath. Of course, a higher percentage extraction of the sulfur was not the primary object sought in this part of the investigation, since it was desired, if possible, not to touch the organic sulfur compounds. Several coals were treated, and the results of these extractions are given below.



Table No. 10

## Hydrochloric-Nitric Acid Extraction of Coal (Per Cent)

Coal No.	Sulfur in Acid Extract	Iron in Acid Extract	Pyritic Sulfur (as calculated from supposed- ly Pyritic Iron*) plus Sulfate sul- fur in Coal	Total Iron in Coal
4	0.89		0.76	
4	0.91		0.76	
8	0.30		0.81	
8	0.29		0.81	
5	0.57	0.44	0.65	0.55
5	0.61	0.48	0.65	0.55
7	2.08	1.58	2.07	1.87
7	2.12	1.58	2.07	1.87
9	0.42	0.50	0.77	0.95
9	0.40	0.52	0.77	0.95
6	3.95	3.34	3.34	3.40
6	3.95	3.29	3.34	3.40

\*Pyritic Iron = Total Iron minus HCl Soluble Iron

Several interesting conclusions may be drawn from this table of data. Without very much doubt the strong solvent action of the hot hydrochloric-nitric acid mixture insured the presence in the filtrate of all the non-silicate iron. We must therefore consider the silicate iron to be the difference between the total iron and that in the filtrate. This difference is shown in the third and fifth columns of the table above. In the case of coals Nos. 7 and 9, the amount of silicate iron is quite large. The error that this would cause in a pyritic sulfur determination





would be rather decided. Another point to be noticed in the above table is that in some cases the sulfur in the extract is higher than that calculated to be present as pyritic and sulfate sulfur. As the existence of silicate iron would make this discrepancy the other way around, the excess sulfur must be part of that organically combined, and oxidized and taken into solution by the strongly oxidizing solvent.

As stated above, the iron extracted by the acid mixture is almost certainly the non-silicate iron, or in other words the sum of the pyritic iron and the iron soluble in dilute hydrochloric acid. If we subtract from this the dilute acid soluble iron, only the pyritic iron will be left and from this can be figured the true amount of pyritic sulfur. In the table below is given a comparison of the percentages of pyritic sulfur by this method, by the old method using the total iron minus the dilute acid soluble iron as representing the pyritic iron, and lastly of the sulfur determined in the hydrochloric-nitric acid extract minus the sulfur soluble in dilute hydrochloric acid.

Table No. 11

Comparison of Pyritic Sulfur Determinations on Coals by  
Different Methods (Per Cent)

	Coal No. 5	Coal No. 6	Coal No. 7	Coal No. 9
Pyritic S from Pyritic Fe. Pyritic Fe=HCL-HNO <sub>3</sub> sol. Fe. minus dilute HCL sol. Fe.	0.30	1.94	1.72	0.25
Pyritic S from Pyritic Fe. Pyritic Fe=Total Fe minus dilute HCL sol. Fe.	0.40	2.03	2.06	0.75
Pyritic S=HCL-HNO <sub>3</sub> sol. S minus dilute HCL sol. S	0.34	2.64	2.09	0.39



It may be seen from this comparison of results that both the pyritic sulfur obtained by the older method of calculation from the total iron and the pyritic sulfur obtained directly from the hydrochloric-nitric acid extraction are higher than that obtained by calculation from the iron soluble in hydrochloric-nitric acid. The high results of the method of calculation from the total iron is due to the presence of greater or less quantities of silicate iron, and the high results of the direct hydrochloric-nitric acid extraction of pyritic sulfur are due to the oxidation of a part of the organic sulfur. A method was now sought in which the oxidation of this organic sulfur would not occur, then the sulfur in whatever extract the process yielded would represent directly the pyritic sulfur (plus the sulfate sulfur) and there would be a distinct line of demarcation between the inorganic and organic forms of sulfur.

The experiments of T. M. Drown on the separate determinations of organic and inorganic sulfur by means of bromine have already been described in this paper. An experiment of this nature was run on Coal No. 9, but the results obtained were as unsatisfactory as with the hydrochloric-nitric acid mixture. Fisher (loc. cit.) had found that the bromine extraction apparently oxidized some of the organic sulfur, and this was also the case here.

A systematic search was conducted for the solvent which would dissolve the pyrites but not the organic sulfur. The scheme used may be briefly outlined as follows. Samples of one of the analysed coals were weighed out and extracted first with dilute hydrochloric acid so as to remove all of the sulfate sulfur and soluble iron. Sometimes the coal was also extracted with phenol,







thereby removing the resinic substances which appear to oxidize rather readily under the action of oxidizing solvents. Any solvent acting on this residue would now take into solution only pyritic iron and sulfur either in the form of pyrites or organic sulfur, since these are the only possible forms left. Of course, concentrated acid solvents acting on the residue for a long time would dissolve out any silicate iron present, but the conditions were always such as to preclude this. The next step, then, was to treat with the solvent for a stated length of time, filter, and analyse the filtrate for sulfur and iron. Now, since the only iron possible of being in the filtrate is pyritic iron, the pyritic sulfur may be figured from this and compared with the sulfur actually in the filtrate. If these two values come out the same, and furthermore this relationship holds for different percentages of iron in the extract, then only one conclusion is possible - that pyritic sulfur and only pyritic sulfur is being taken into solution.

The first experiment tried was preliminary, and was a check determination using iron pyrites. A small quantity of finely powdered crystalline iron pyrites was mixed with some of coal No. 3. This coal was chosen because it was a very low sulfur coal and would furnish the coal substance proper with very little organic sulfur to interfere. This was first extracted with dilute hydrochloric acid to remove all soluble iron and sulfur. The mixture now corresponded to a high sulfur coal, with nearly all of the sulfur present as pyrites. One half gram samples of this were extracted with 15 c.c. of hydrochloric-nitric acid mixture for a few minutes, diluted, filtered, and the filtrate analysed for iron and sulfur. The results obtained, expressed in percent-



ages of the original weight of sample, are as follows:

Table No. 12

Extraction of Coal-Iron Pyrites Mixture with Hydrochloric-

Nitric Acid (Per Cent)

Sample No.	Iron in Acid Extract	Sulfur in Acid Extract	Pyritic Sulfur Cal- culated from Iron in Acid Extract as Pyritic Iron
1	1.67	1.94	1.91
2	1.34	1.53	1.53
3	1.30	1.44	1.48
4	1.30	1.51	1.48

The different amounts of iron in the extracts result from the difference in violence of the beginning of the reactions, which were allowed to proceed for only a few minutes, and are advantageous rather than otherwise since they show that it is iron pyrites that is being extracted during every phase of the reaction. The similarity between the amount of sulfur in the acid extract and the amount as calculated from the iron in the acid extract leave no doubt as to this fact.

The next experiment was performed with coal No. 7. The effect of the hydrochloric-nitric acid treatment on this is shown in the following table. The extractions were allowed to proceed for different lengths of time, so that varying quantities of pyrites would be extracted.





Table No. 13

Extraction of Coal No. 7 with Hydrochloric-Nitric Acid

(Per Cent)

Time of Extraction	Iron in Acid Extract	Sulfur in Acid Extract	Pyritic Sul- fur Calculated from Iron in Acid Extract as Pyritic Iron
1 min.	0.30	0.37	0.34
2½ min.	0.53	0.76	0.61
5 min.	0.54	0.90	0.62
10 min.	0.77	1.32	0.88

This table shows experimentally what has been intimated before, - that as strong an oxidizing solution as hydrochloric-nitric acid not only attacks the pyrites but also oxidizes the organic sulfur. It may be noticed how the difference between the figures in the last two columns becomes greater as the time increases, which would show that the rate of oxidation of the organic sulfur is rather slow.

On Plate II, this relationship is expressed graphically by the series of curves. The curve representing the sulfur in the acid extract rises much faster than the curve showing the sulfur which should be there if only pyrites were being taken into solution, using the amount of iron dissolved as a measure of the pyrites.

The next table shows the effect of concentrated nitric acid alone on coal No. 7.



Per Cent in Extract

1.50

1.25

1.00

.75

.50

.25

0

S in Extract

FeS<sub>2</sub>Theoretical S for FeS<sub>2</sub>

Fe in Extract

## PLATE II

CONCENTRATED HYDROCHLORIC-NITRIC ACID  
EXTRACTION OF COAL NO. 7

Curves Showing Relation Between Sulfur  
Extracted and Sulfur Which Would Com-  
bine With Iron in Extract to Form FeS<sub>2</sub>

Time in Minutes

4 5

6

7

8

9

10

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Table No. 14

Extraction of Coal No. 7 with Concentrated Nitric Acid.

(Per Cent)

Time of Ex- traction	Iron in Acid Extract	Sulfur in Acid Extract	Pyritic Sulfur Cal- culated from Iron in Acid Extract as Py- ritic Iron.
2½ min.	0.90	1.05	1.03
5 min.	1.04	1.18	1.19
10 min.	1.05	1.16	1.20

These results would make it appear as though concentrated nitric acid was the solvent sought for. However, using two gram samples of the coal and allowing the extraction to proceed for a longer time yielded the following results.

Table No. 15

Extraction of Coal No. 7 with Concentrated Nitric Acid.

(Per Cent)

Time of Ex- traction	Iron in Acid Extract	Sulfur in Acid Extract	Pyritic Sulfur Cal- culated from Iron in Acid Extract as Py- ritic Iron.
1 min.	0.92	1.18	1.05
15 min.	1.01	1.35	1.15
30 min.	0.99	1.36	1.13
60 min.	1.00	1.36	1.14

Concentrated nitric acid will therefore attack the organic sulfur compounds as shown by the difference between the figures in the last two columns, and would not make an ideal solvent for the iron pyrites.

It was found much more convenient in experiments of this



kind to extract a quantity of the coal with dilute hydrochloric acid and then weigh out portions of this for the various solvent treatments, instead of taking the time to extract each sample separately. The analysis of some of these extracted coals is given below.

Table No. 16

Sulfur and Iron Content of Coals after Extraction with  
Dilute Hydrochloric Acid (Per Cent)

Coal No.	Total Iron	Total Sulfur
5	0.44	1.08
6	2.22	4.00
7	1.62	3.13

Unless otherwise mentioned, the hydrochloric acid extracted samples were used from this point on. As a general rule, one gram samples of these treated coals were taken for the extractions, this being the amount used in the extraction experiments just described.

In the next experiment, an effort was made to slow down the violent initial reaction between the nitric acid and the coal, in this way hoping to attack the organic sulfur less. The concentrated nitric acid was diluted with an equal volume of water and was added to the coal almost ice-cold. The results obtained follow, using Coal No. 6.





Table No. 17.

## Extraction of Coal No. 6 with Cold Nitric Acid (Per Cent)

Time of Ex- traction	Iron in Acid Extract	Sulfur in Acid Extract	Pyritic Sulfur Calculated from Iron in Acid Ex- tract as Pyritic Iron
1 min.	1.67	1.97	1.91
15 min.	1.72	2.11	1.97
30 min.	1.72	2.25	1.97
60 min.	1.76	2.30	2.01

The excess of sulfur in the extract clearly indicates that even under the conditions of this experiment the organic sulfur is oxidized.

Results Obtained with Dilute Nitric Acid as Solvent

Samples of coal No. 7 extracted with various dilutions of nitric acid for about 20 minutes. In the following table of results, the first column gives the number of volumes to which one volume of concentrated nitric acid was diluted.

Table No. 18.

Extraction of Coal No. 7 with Various Dilutions of  
Nitric Acid (Per Cent)

Dilution	Iron in Acid Extract	Sulfur in Acid Extract	Pyritic Sulfur Calculated from Iron in Acid Extract as Pyritic Iron
1	1.09	1.43	1.24
2	1.13	1.32	1.29
4	0.62	0.67	0.71
8	0.25	0.24	0.29



The last two dilutions gave very little sulfur in the extract and are probably a little low. The dilution of 2 gave rather good results, but the dilution of 4 appeared to be the strongest acid which seemed to have no oxidizing effect on the organic sulfur. In other words, this experiment showed that concentrated nitric acid diluted to four times its volume possessed the maximum solvent effect on iron pyrites, without attacking the organic sulfur. All subsequent extractions for pyritic sulfur were made with this strength of nitric acid.

The next table gives the results obtained by the use of this solvent on various hydrochloric acid extracted coals. All were treated at room temperature.

Table No. 19

Extraction of Coals with Dilute Nitric Acid (Per Cent)				
Coal No.	Time of Extraction	Iron in Acid Extract	Sulfur in Acid Extract	Pyritic Sulfur Calculated from Iron in Acid Extract as Pyritic Iron
7	1 hr.	1.12	1.23	1.28
7	18 hrs.	1.16	1.29	1.33
7	72 hrs.	1.13	1.30	1.29
7	10 days	1.20	1.36	1.37
6	4 days	1.80	2.06	2.06
6	4 days	1.80	2.06	2.06
5	4 days	0.27	0.31	0.31
5	4 days	0.27	0.31	0.31
9	4 days	0.15	0.16	0.17
9	4 days	0.15	0.16	0.17
10	4 days	0.08	0.10	0.09
10	4 days	0.08	0.10	0.09

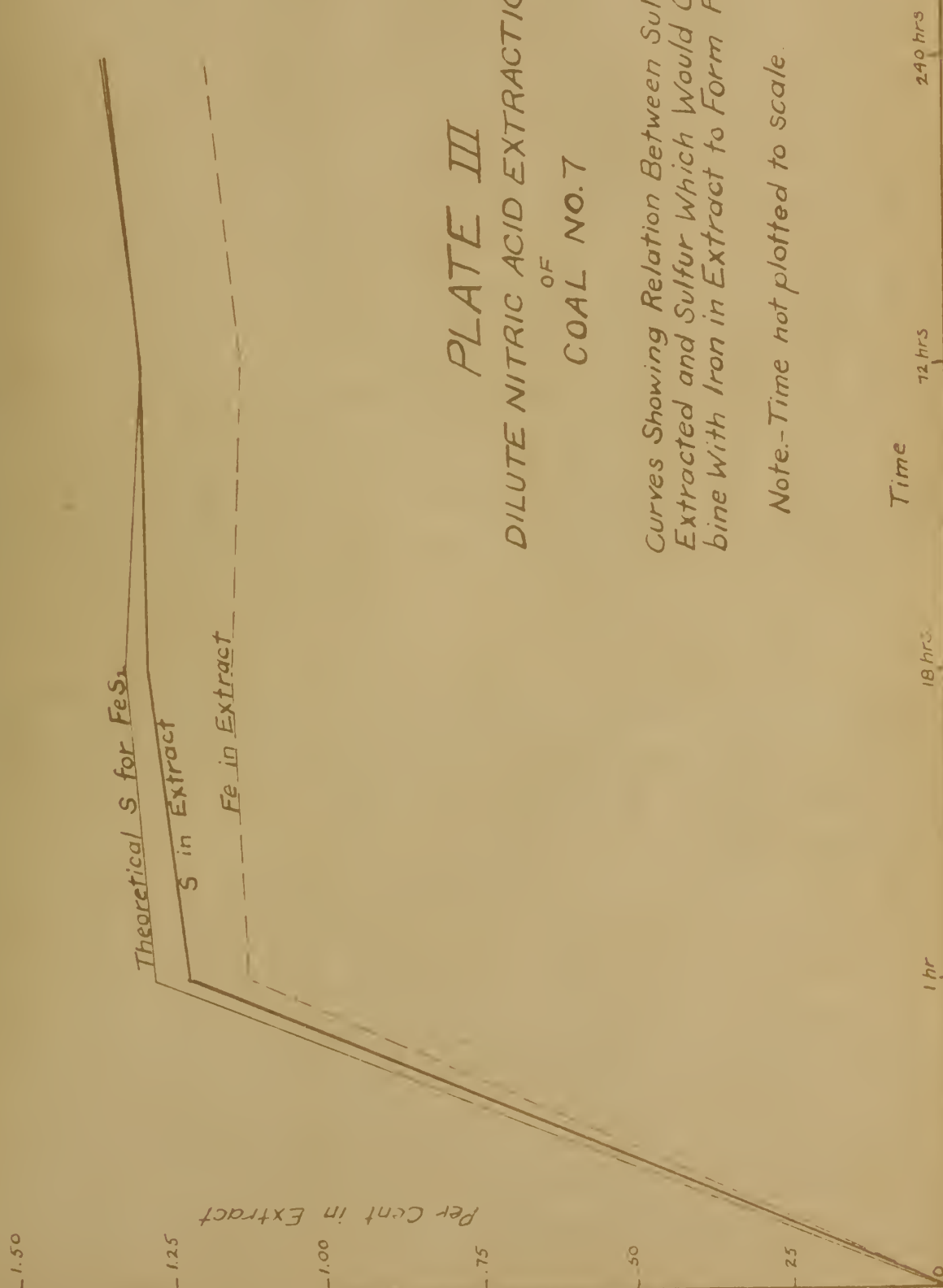


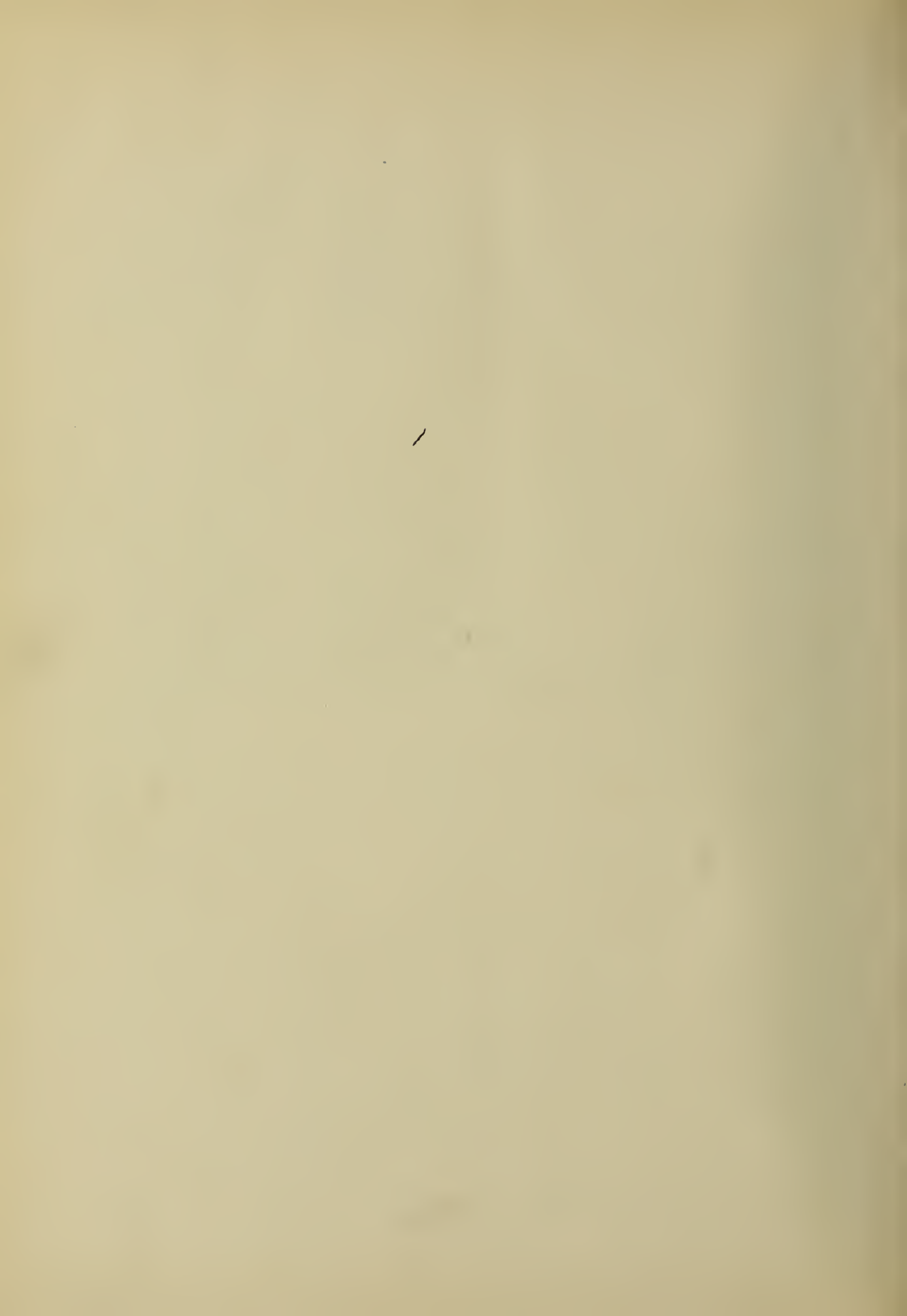


# PLATE III DILUTE NITRIC ACID EXTRACTION OF COAL NO. 7

Curves Showing Relation Between Sulfur  
Extracted and Sulfur Which Would Com-  
bine With Iron in Extract to Form  $\text{FeS}_2$

Note.—Time not plotted to scale.





Although the coals extracted were of several types and of widely varying sulfur content, the amount of sulfur in the extract and the amount of sulfur calculated to make  $\text{Fe S}_2$  were in every case remarkably close together, as shown by the last two columns of the above table. The dilute nitric acid is therefore a selective solvent for iron pyrites. The relationship between the sulfur extracted by the acid and the pyritic sulfur as calculated from the iron extracted by the acid is shown graphically for coal No. 7 by the curves on Plate III.

In order to determine the best conditions for the dilute nitric acid extraction, the following experiment was performed. Three samples of coal No. 7 were extracted with the dilute nitric acid; one was boiled for 15 minutes, another was heated on the steam bath for 4 hours, while the third was allowed to stand at room temperature for four days. The following results were obtained.

Table No. 20

## Extraction of Coal No. 7 with Dilute Nitric Acid (Per Cent)

Conditions of Extraction	Iron in Acid Extract	Sulfur in Acid Extract	Pyritic Sulfur Calculated from Iron in Acid Extract as Pyritic Iron
Boiled for 15 minutes	1.06	1.49	1.21
Steam bath for 4 hours	1.14	1.58	1.30
Room Temp. for 4 days	1.14	1.32	1.30

This shows that the quantitative extraction of the pyritic sulfur can be brought about by no other method than treatment at room temperature for several days. Any attempt to hasten the process by heat would result in the oxidation of some of the or-





ganic sulfur.

The Determination and Identification of Humus Sulfur  
in Coal.

The experiments on the phenol extraction of coal had proven that a certain portion of the sulfur existed in the resinic type of material in organic combination. The dilute hydrochloric acid extraction had been the means of determining the sulfate sulfur. Lastly, the dilute nitric acid had quantitatively removed the pyritic sulfur from the coal. However, on adding up the percentage compositions of these three known forms and subtracting from the total sulfur, quite a quantity of sulfur was shown to be still unaccounted for. Any possibility that this extra sulfur could be combined with the iron to form a higher sulfide than  $\text{Fe S}_2$  was eliminated by the nitric acid extraction experiments. Some other type of compound was therefore sought.

About five grams of coal No. 7 were extracted with concentrated nitric acid at room temperature for 24 hours. This treatment removed the pyritic and sulfate sulfur, but left nearly all of the remainder in the residue, so that the latter could be studied conveniently by itself. Further treatment of the residue with nitric acid yielded no sulfur in the filtrate whatever, and neither did boiling dilute nitric acid have any effect.

Guignet and later Friswell (loc. cit.) had both observed the effect of alkalies on coal previously treated with nitric acid. Portions of the nitric acid residue were placed in beakers, and one was treated with 25 c.c. of concentrated aqua ammonia, the other with a concentrated sodium peroxide solution. In both cases,



the thick dark brown solution described by Friswell was formed. The ammonia extract was diluted and filtered, the filtrate having a dark reddish brown color. Upon acidifying a portion of this filtrate with hydrochloric acid, a brown flocculent precipitate formed, and this was filtered off with the same difficulty which characterized the first filtration. The filtrate in this case was a very light yellow in color and contained no sulfur, showing that the sulfur in the nitric acid residue must be present in either the ammonia insoluble substance, of which there was very little compared to the original residue, or else in the flocculent brown precipitate. The qualitative analysis of this precipitate, sometimes referred to in the literature as the "coal acid" showed large quantities of sulfur. Furthermore, an analysis of the small undissolved portion of the residue gave but a trace of sulfur. Anderson and Roberts (loc. cit.) had found that this undissolved portion consisted of about 60 per cent organic matter very similar to the coal acid which would have gone into solution had it not been occluded. This could easily account for the trace of sulfur found. From this experiment, it was concluded that a knowledge of the unknown form of sulfur depended on a study of the coal acid. The results of the sodium peroxide extraction were similar to those obtained by the ammonia.

The next problem to be attacked was as to whether the unknown form of sulfur was organic or inorganic in nature. The most logical method of accomplishing this purpose was the study of the ash of the coal acid. Two grams of coal No. 7 were treated in the usual manner, and this resulted in the formation of over 1.5 grams of ammonia soluble material. This was ashed in a plati-







num crucible, and the percentage of ash figured on the basis of the original coal was 0.35 per cent. The ash content of the original coal was 9.45 per cent, which shows that only a very small part of the mineral matter is extracted by the ammonia. The ash was then treated with hydrofluoric acid and sulfuric acid to get rid of the silica and on heating to change the metals present to the oxides. This mixture of oxides was dissolved and analysed for iron. By this method, the ash analyses are as follows:

Silica	0.10 per cent
Fe <sub>2</sub> O <sub>3</sub>	0.05 per cent
Other oxides	<u>0.20</u> per cent
Total Ash	0.35 per cent

The unknown sulfur which was present in the ammonia extract amounted to about 1.00 per cent. It is inconceivable that this amount of sulfur could be combined in some inorganic compound while the mineral matter was present in such a small amount. Moreover, it is highly improbable that if such a compound should exist, it would resist the action of concentrated nitric acid and then dissolve in ammonia. The conclusion is therefore drawn that this sulfur is of an organic nature, that it exists in the humus like portion of coal described in the literature, and that its combination in such substances is extremely stable. Because of the nature of the body in which it occurs, this form of sulfur is referred to hereafter as humus organic sulfur in order to differentiate it from the resinic organic sulfur.

It now became necessary, in order to absolutely prove the methods just given, to determine the amounts of the various forms of sulfur present in certain coals, add these together and see



how closely the total checked the total sulfur of the coal as determined by sodium peroxide fusion. Extremely close checks were not looked for, since the combined errors of five determinations entered into each comparison. The following table gives the average results obtained on five different coals, which were all that were studied in this connection.

Table No. 21

Analyses of Different Forms of Sulfur in Coals and Comparison with Total Sulfur ( Per Cent )

Coal No.	4	5	6	7	8
Resinic Sulfur	0.34	0.16	0.77	0.50	0.10
Sulfate Sulfur	0.05	0.25	1.31	0.31	0.01
Pyritic Sulfur	0.85	0.31	2.06	1.36	0.29
Humus Sulfur	0.87	0.51	0.70	0.95	0.45
Total	2.11	1.23	4.84	3.12	0.85
Total S by $\text{Na}_2 \text{O}_2$ fusion	2.14	1.20	5.00	3.31	1.02
Difference between totals	0.03	0.03	0.16	0.19	0.17

Considering the long series of manipulations which were necessary to obtain the sum of the four sulfur forms, the agreement between the two totals in each case is very satisfactory. The last three gave low results which was probably due to the retention of some of the humus sulfur by the residue when the ammonia extraction was performed. This was particularly true of coal No. 8, which dissolved in the ammonia with great difficulty after the nitric acid treatment. However, the results obtained by the various extraction methods prove the general character of all the sulfur of the coal.







Several attempts were made to arrive at a more specific knowledge of the organic sulfur compounds present in coal, but negative results were obtained in every case. Smiles' test for sulfuric acids and sulfoxides was performed by treating some finely powdered coal with concentrated sulfuric acid and then adding a drop of anisole. The same test was applied to some of the ammonia extract, but in neither case was the positive blue color obtained. The isatin test for thiophen also gave negative results. It is very probable that both the resinic and the humus types of organic sulfur compounds are of a decidedly complex nature.



Conclusions. First. The sulfur of coal occurs in four characteristic forms, two of them organic and the other two inorganic.

(a). The resinic organic type is shown to be organic sulfur by its lack of an ash, and its presence in that portion of the organic material soluble in phenol indicates its association with that substance.

(b). The humus organic sulfur is shown to be organic by the very small amount of ash in the compounds in which it occurs and these compounds are shown to be closely related to humus substances by their chemical action.

(c). The pyritic or marcasite sulfur is present as  $\text{Fe S}_2$  as indicated by the iron-sulfur ratio when the pyrites is oxidized and taken into solution.

(d). The sulfate sulfur is shown to be such by the fact that it dissolves in dilute hydrochloric acid as sulfate without preliminary oxidation. All four forms have therefore been definitely proven present.

Furthermore, these forms of sulfur are the only ones existing in the coal. This is shown by the fact that the combined percentages account for all of the sulfur. Free sulfur in coal was not found in any of the samples worked upon and is presumably absent except in unusual cases, where it might occur in small quantities as a decomposition product of pyrites.

Second. Methods have been developed for the quantitative analysis of each form of sulfur. The following is a brief statement of the methods used in determining each kind of coal sulfur.





(a). The sulfate sulfur is determined by extraction of the coal with dilute hydrochloric acid.

(b). The pyritic sulfur is determined by extraction of the coal with dilute nitric acid, after a preliminary extraction with dilute hydrochloric acid to remove the sulfate form.

(c). The resinic sulfur is determined by extraction of the coal with phenol.

(d). The humus sulfur is determined by the difference between the sum of the other three forms and the total sulfur in the coal. Or, a direct determination may be made by extraction of the coal with ammonium hydroxide, after a preliminary treatment with concentrated nitric acid.

Third. The older method of determining the forms of sulfur in coal gives high results for the pyritic sulfur and low results for the organic sulfur. This is due to the assumption that all of the iron not soluble in dilute hydrochloric acid is pyritic sulfur. In some cases this false assumption makes the percentage of pyritic iron several times as high as it should be. The method developed in this investigation is by far the most accurate one found for the analysis of the different forms of sulfur in coal.



## III

Changes in the Forms of Sulfur in Coal on Standing  
or by Oxidation

Introduction and Historical. When coal is allowed to remain exposed to the air for any length of time, certain fundamental changes take place, the exact nature of which has been determined only partially. Since these changes affect the heating and coking value of the coal to quite an extent, numerous investigations have been carried on in order to learn the conditions which will best prevent their occurrence.

Parr and Hamilton<sup>47</sup> have reviewed some of the work done with regard to this problem and from their own observations have come to the following conclusions:

- a. Submerged coal loses no heat value.
- b. Outdoor exposure causes loss of 2 to 10 per cent.
- c. High sulfur coals oxidize in the open more than under cover, as the oxidation of the sulfur promotes other disintegration.
- d. The main loss occurs in the first 5 months.

Even when coal samples were sealed tightly so as to eliminate all exposure to air, much of the same deterioration occurs. Parr and Wheeler<sup>48</sup> have shown that the heating value of coal kept under these conditions may decrease as much as 4.3 per cent. Gases seem to be given off continually, but with the greatest volume during the first two or three weeks of storage. Oxidation also occurs, due probably to the absorption of some oxygen.





In the present investigation one of the most noticeable features was the rapid change of certain sulfur forms to sulfate. An extreme example of this was the coal known as No. 6 having a sulfur content of 5 per cent. After standing in a tightly stoppered Erlenmeyer flask for two years, the amount of sulfate sulfur had increased from less than 0.01 per cent to 1.31 per cent. As the soluble iron had increased greatly also, it appeared that the pyrites was being oxidized in some manner. It was with reference to this sulfur oxidation that the following experiments were carried out.



### Experimental

At first some investigation was conducted as to the most favorable conditions for this coal sulfur oxidation to occur. 5 grams of coal No. 1 were placed in the bottom of an Erlenmeyer flask. A tube leading nearly to the bottom of the flask was connected to a U tube filled with thoroughly moistened glass wool. A slow current of air was passed through the U tube and thence into the flask, so that the finely powdered coal was at all times exposed to fresh moist air. The flask containing the coal was kept in the electric oven for 18 hours which was regulated so as to maintain a constant temperature of 60 degrees. Also, in order to compare the effect of moist and dry air, another run was made in which the U tube was filled with calcium chloride instead of the moist glass wool. The following table gives the results obtained:

Table No. 22

Oxidation of Coal Sulfur by Moist and Dry Air.

(Per Cent)

Total Sulfur in Coal	2.68
Sulfate Sulfur in Coal	0.045
Sulfate Sulfur in Coal after Oxidation by Moist Air	0.207
Sulfur Oxidized by Moist Air	0.162
Sulfate Sulfur in Coal af- ter Oxidation by Dry Air	0.173
Sulfur Oxidized by Dry Air	0.128





These results showed that a comparatively small portion of the coal sulfur was oxidized under the most favorable conditions as regards supply of air, temperature, and fineness of division, the only unfavorable condition to a very large amount of oxidation being the short time of exposure. It would appear, then, that either the oxidation of the sulfur was a time process or else that some other factor than simple chemical oxidation entered into the change. It is to be noted that the moist air causes a larger amount of sulfate sulfur to be formed than the dry air.

An attempt was made to arrive at some conclusion as to the nature of the sulfur oxidation process. The experiment just described would tend to show that the oxidation of the coal sulfur was not a simple reaction in which an excess of air would cause a proportionally greater change than that which would occur in a closed flask. A possible explanation for this would be that certain anaerobic bacteria were present in the coal causing the gradual oxidation of the coal sulfur in the absence of a free access of air. The following experiment was designed to test this out.

Coal No. 7 was chosen as the medium to carry out the tests since this was a comparatively fresh coal with a low sulfate content and a high percentage of pyrites. If bacteria were the cause of the change, they would be found in the largest quantity in a coal where a very decided sulfur oxidation had occurred. As mentioned before coal No. 6 had this property, so this was chosen as the inoculating agent. Four small flasks were fitted with rubber stoppers covered with tin foil from which were suspended glass hooks to support some wet cotton, so that the interior of the flask would be continually moist. In two of these there was



placed 5 grams of coal No. 7, finely powdered, in the other two 4 grams of coal No. 7. All four flasks were thoroughly sterilized in a steam autoclave.

After sterilization, one gram of coal No. 6 was added to each of the two 4-gram flasks. There were now two flasks containing sterile coal and two others containing sterile coal mixed with a smaller quantity of old heavily oxidized coal. The set of flasks was kept at a constant temperature of 37 degrees and the contents later analysed for the hydrochloric-acid-soluble sulfur and iron. In order to find out how much the sulfur of coal No. 6 itself increased, two flasks containing one gram each were made up as controls to keep with the others. Analyses of the flask contents were made 19 days after placing in the incubator room and another set of analyses 88 days after.

From this data the increase in soluble sulfur and iron in all flasks was calculated. Since the sterile flask contained 5 grams of coal, this increase was multiplied by four-fifths in order to get down to a basis of 4 grams and then the increase in the control flask added to this. If the process were a simple chemical reaction, this last figure should be equal to the increase in the other flask, since this latter was made up of 4 grams of sterile coal and one gram of coal No. 6. If, however, the action of bacteria entered into the change, we should expect a larger increase of soluble sulfur and iron in the flask where the sterile and the inoculated coals were in contact than in the sum of the increases where the two were kept separate. The following table gives the results obtained.







Table No. 23

Relative Oxidation of Pyrites in Sterile and Inoculated  
Coals. (Milligrams)

	19 days	88 days
Increase of sol. sulfur in 4 g. steril coal No. 7	11.88 mg.	14.00 mg.
Increase of sol. sulfur in 1 g. coal No. 6	4.40 "	9.40 "
Calculated increase of sum of above	16.28 "	23.40 "
Actual increase of sol. sulfur by analysis	16.40 "	34.70 "
Increase of sol. iron in 4 g. sterile coal No. 7	14.05 "	15.00 "
Increase of sol. iron in 1 g. coal No. 6	5.55 "	10.40 "
Calculated increase of sum of above	19.60 "	25.40 "
Actual increase of sol. iron by analysis	19.70 "	38.00 "

At the end of 19 days there apparently was nothing unusual in the relative oxidation of sulfur in the sterile and in the inoculated coal. At the end of 88 days, however, the inoculated coal had shown quite a decidedly greater increase than the sterile coal. The only explanation for this would be some bacteriological action or perhaps catalysis. Another interesting point to be noted here is that the soluble iron shows a greater increase than the soluble sulfur in every case whether the coal be sterile or not. If only pyrites were being oxidized, there would be one and one-seventh times as much sulfur as there was iron, and if other sulfur forms were oxidized the ratio would be still larger. However, in actual practice the opposite is true. The best explanation for this is that some of the sulfate formed is taken up by the organic matter of the coal.



### Conclusions

First. Some of the coal sulfur, probably the iron pyrites is oxidized gradually to the form of sulfate.

Second. One of the chief factors in this reaction seems to be time. An excess of air has no very decisive effect, in fact, a great deal of oxidation occurs in a coal kept in a tightly stoppered flask.

Third. The reaction seems to be hastened by the presence of bacteria or some catalytic agent. This influence is not evident at first due perhaps to the large amount of free oxygen in the flask at that time.

Fourth. The amount of soluble sulfate formed is less than it should be if we take the soluble iron as a criterion. This points to the union of some of the oxidized sulfur with the organic matter of the coal.

Fifth. The results obtained indicate that a further study of coal sulfur oxidation would not be without profit.





## IV.

Changes in the Forms of Sulfur in Coal on Coking

Introduction and Historical. When coal is subjected to destructive distillation in the absence of air, the sulfur divides itself between the residue and the volatile matter. The ratio between the residual sulfur and the volatile sulfur varies between rather wide limits but is fairly constant for the same coal. Just what factors in the coal control this ratio have not yet been determined except in a very general manner. Certain coal constituents entirely separate from the sulfur containing compounds may have an effect on the percentage of sulfur retained in the coke, but in all probability the most decisive factor is the relative amount of the different sulfur forms present. As the first part of this investigation has furnished a good means for determining these sulfur forms, their effect on the proportion of residual sulfur in coking was studied.

Furthermore, the types of sulfur compounds formed in the coke were subjected to investigation, and some relation sought between the quantities of these types formed in the coke and the quantities of the different types of sulfur in the coal. Since the forms of sulfur in coke are entirely different from those in coal, this latter problem involved an entirely new method of attack.

In 1910 M'Callum conducted an investigation to determine the effect of different percentages of organic and inorganic sulfur in the coal on the amount of residual sulfur when the coal was coked.<sup>49</sup> The coal used was from Nova Scotia. It was finely ground and then separated into different fractions by using solu-



tions of different specific gravities. By this method, five fractions were obtained and analysed for organic and inorganic sulfur content. This was done by calculating the sulfur which would unite with the total iron to form pyrites and calling this the inorganic sulfur. The rest of the sulfur was taken as organic. The writer claimed that no sulfate sulfur was present and he believed that silicate iron was so low as to make no difference. He apparently did not determine the dilute-hydrochloric-acid-soluble iron. With these very evident sources of error in his scheme of analysis, however, he found that the five fractions varied in organic sulfur content from 37 per cent of the total sulfur to 85 per cent.

Each of these samples was then coked so as to get the relative amounts of volatile and residual sulfur. Where the organic sulfur was present as 37 per cent of the total sulfur, the volatile sulfur ran 33 per cent, and where the organic sulfur was 85 per cent, the volatile sulfur was 52 per cent. No definite relationship seemed to exist between the amount of organic sulfur and the volatile sulfur, except that, in general, where the organic sulfur was high, the volatile sulfur was also high. This experiment seemed to disprove one of the old theories that coking a coal drove out all of the organic sulfur and one-half of the pyritic. His conclusion was that "a very considerable part of the organic sulfur is volatilized".

Bradbury<sup>50</sup> as early as 1878 studied the forms of sulfur in coke. He treated the finely powdered coke with dilute hydrochloric acid and collected and determined all of the hydrogen sulfide given off. The dilute hydrochloric acid solution was analysed for sulfate sulfur and for iron. The residue was then treated with







concentrated aqua regia and potassium chlorate and this solution also analysed for sulfur.

His results showed that only a small portion of the total sulfur of the coke existed as sulfide sulfur, that practically none existed as sulfate sulfur, and that even the strong oxidizing influence of the aqua regia-potassium chlorate mixture failed to take out more than a small part of the total sulfur. From these results he concluded that the larger part of coke sulfur was in an organic form. Practically all of the iron of the coke was dissolved by the dilute hydrochloric acid showing that the iron pyrites of the original coal had been completely decomposed during the coking process.

### Experimental

The first experiments tried were simply with regard to the amount of residual sulfur. To determine this, a one-gram sample of the coal to be tested was coked in a small nickel crucible. This was heated for three and one half minutes at the full heat of the Bunsen burner and then for another three and one half minutes with a blast lamp. A tight fitting nickel cover prevented oxidation of the coal. The coke was carefully removed and pulverized, after which it was fused with sodium peroxide in the same manner as the coal had been in another part of this investigation. After the fusion had been dissolved in water, the sulfur was determined by means of the barium sulfate precipitation. Some of the coals used in this work were the original samples, while other experiments were run with samples which had previously been extracted with dilute hydrochloric acid so as to remove all of the sulfur in



the form of sulfate. In the table below, due allowance is made for this removal of the sulfate form in the amount of total sulfur.

Table No. 24

Forms of Sulfur in Coal and Residual Sulfur Left after  
Coking. (Per Cent)

Coal No.	5a	6a	7	7a	10	10a
Total Sulfur	1.08	4.00	3.31	3.00	0.95	0.93
Sulfate Sulfur	0.00	0.00	0.31	0.00	0.02	0.00
Pyritic Sulfur	0.31	2.06	1.30	1.30	0.10	0.10
Resinic Sulfur	0.16	0.77	0.50	0.50	0.13	0.13
Humus Sulfur	0.61	1.17	1.20	1.20	0.70	0.70
Residual Sulfur	0.34	1.46	1.37	1.09	0.45	0.38

Those coals having "a" after the number in the above table are the ones which were previously extracted with dilute hydrochloric acid before coking. Comparing these coals with the corresponding coals which had not been extracted, it is interesting to note the difference between the amounts of residual sulfur in each case. In coal No. 7 this difference almost corresponds to the sulfur which had been removed by the dilute hydrochloric acid. However, in the case of coal No. 10, the difference is somewhat greater than the sulfate sulfur. A very reasonable explanation for this would be that coal No. 10 contained calcite, which on heating would change to calcium oxide and this would unite with some of the hydrogen sulfide which ordinarily would volatilize. Where the coal had previously been extracted with acid, however, the calcite would be removed and therefore the residual sulfur would be less.

A very cursory study of the table will show the falsity of the theory that all of the organic and one half of the inorganic







sulfur are volatilized during coking. In order to get some idea of the proportion of the various sulfur forms left in the coke, the following calculations were performed. Coals Nos. 6a, 7a, and 10a were chosen since these contained more of the sulfate form to complicate the calculations and also they would be free of calcite which might enter into a secondary reaction with some of the volatile sulfur as explained previously. There would then be three unknown quantities of residual sulfur to add up to the total residual sulfur which was known. Then,

Let X = fraction of pyritic sulfur left in coke

Y = " " resinic " " " "

Z = " " humus " " " "

For coal No. 10a,  $.1X$  plus  $.13Y$  plus  $.7Z = .38$

For coal No. 6a,  $2.06X$  plus  $.77Y$  plus  $1.17Z = 1.46$

For coal No. 7a,  $1.30X$  plus  $.5Y$  plus  $1.20Z = 1.09$

Solving these equations simultaneously, the results are as follows,

Pyritic sulfur left in coke 16 per cent.

Resinic sulfur left in coke 95 per cent.

Humus sulfur left in coke 34 per cent.

These figures would probably not hold for every coal since undoubtedly other factors enter into the retention of the sulfur in the coke. However, they are interesting as showing that rather a large amount of the organic sulfur is retained.

The retention of so much of the organic sulfur led to some experiments on the nature of the sulfur compounds in the coke. Although Bradbury (loc. cit.) had believed the large portion of the coke sulfur to be organic in nature, it was difficult to conceive of



any organic compound withstanding the high temperature of the coking process. A more reasonable explanation would be that secondary reactions caused the organic sulfur to change over into some very stable inorganic form.

The problem was attacked by much the same methods that Bradbury had used. The finely powdered coke was placed in a small flask. This flask was so arranged that hydrogen could bubble through a liquid in the bottom and pass out at the top into an absorption tower containing a rather strong sodium peroxide solution. The coke from one gram of the original coal was used and over this was poured about 40 c.c. of dilute hydrochloric acid (1 part HCl, sp. gr. 1.19 to 1 part water). A slow stream of hydrogen was then conducted through the apparatus for about one hour, and finally the solution in the flask was brought to boiling to insure the removal of all of the hydrogen sulfide.

By this method, any sulfate sulfur in the coke would go into solution and the sulfide sulfur would be carried over in the stream of hydrogen as hydrogen sulfide and be oxidized to sodium sulfate in the sodium peroxide tower. Therefore, by barium sulfate precipitation both the sulfate and sulfide forms of sulfur in the coke could be determined. The residue of this extraction was then treated with concentrated nitric acid for two hours in order to extract any pyrites that might be left. The results of this experiment on coal No. 7 are given in the table below together with a comparison to the forms of sulfur in the original coal. The percentages of sulfur and iron in the coke are figured on the basis of the weight of original coal used, so that a direct comparison may be made with the coal.







Table No. 25

Forms of Sulfur in Coke Compared with Original Coal.

(Per Cent)

	Coal No. 7	Coke from Coal No. 7
Total Sulfur	3.31	1.37
Sulfate Sulfur	0.31	0.00
Sulfide Sulfur	0.00	0.30
Pyritic Sulfur	1.30	0.00
Resinic Sulfur	0.50	0.00
Humus Sulfur	1.20	0.00
Unknown Sulfur	0.00	1.07
Total Iron	1.87	1.87
Soluble Iron	0.41	1.04
Pyritic Iron	1.13	0.00
Silicate Iron	0.33	0.83

The results show that the larger part of the sulfur of the coke is as yet undetermined as to structure. The concentrated nitric acid treatment removed only 0.07 per cent, so that the compound or compounds in which it is present must be very stable. The possibility of a carbon-silicon-sulfur compound presented itself, but all of such compounds in the literature either decompose in the presence of water or of hydrofluoric acid, releasing hydrogen sulfide. No hydrogen sulfide could be detected even when the finely powdered residue of the above extraction was boiled with hydrofluoric acid. It seems therefore not to be an iron-sulfur compound, neither is it a silicon-sulfur compound. So far as present data are concerned it would seem to be a carbon-sulfur compound, the nature of which is as yet undetermined.



After the finely powdered coke had been boiled with dilute hydrochloric acid to release the sulfide sulfur as hydrogen sulfide the residue was further treated as follows. A quantity of fine aluminum turnings and some more dilute hydrochloric acid were added and the mixture again heated. Under these conditions, a large amount of hydrogen sulfide came off. This action of nascent hydrogen on the coke would indicate still further the organic or carbon-sulfur character of this portion of the coke sulfur.

We have other illustrations of the fact that certain carbon compounds persist through the high temperature condition to which coal is subjected in the coking process. For example, the treatment of red hot coke with water vapor releases a large amount of nitrogen as  $\text{NH}_3$  which was held in some chemical combination with the carbon. In addition to ammonia, hydrogen sulfide is released from the coke by the same treatment. During the coking process, hydrogen compounds persist up to and beyond a temperature of 1000 degrees. These well known facts show that it is possible for nitrogen, sulfur and hydrogen to remain in organic combination at very high temperatures.

It has been stated previously that the coal material extracted by phenol consists entirely of organic matter of a resinic nature. In order to investigate the sulfur distribution during coking in this type of material, one gram of the extracted substance from coal No. 7 was coked under standard conditions. By this experiment it was found that 50 per cent of this form of organic sulfur was retained in the coke. This proved definitely that a portion of the coke sulfur was organic both as to its character and source.





Some of the changes in the table above are worthy of comment. The sulfate sulfur disappears entirely, due to the reducing influence of the red hot coal but it does not change to the sulfide form, as will be shown later. It probably goes over to the unknown form of sulfur, since it has already been shown that the residual sulfur is higher if the sulfate is not extracted with hydrochloric acid before coking. The source of the sulfide sulfur will be explained later. The pyritic sulfur is entirely decomposed during the coking process.

Both of the organic forms of sulfur in the coal change from their original form. This is shown by the fact that phenol has no effect on the coke and also that ammonia will not dissolve the nitric acid residue, both of which are characteristic properties of the two sulfur forms in the coal.

Some of the changes in the forms of iron during the coking process are also indicative of important changes. The acid soluble iron increases greatly. This would be expected if all of the pyrites decomposed. The decomposition of the pyrites also leads to quite a decided increase in the content of iron silicate.

The source of the sulfide sulfur in the coke was subjected to some investigation. Four one gram samples of coal No. 7 were extracted with dilute hydrochloric acid and two of these were further extracted with phenol. The residues were coked and then the sulfide sulfur determined as in the previous experiment. The original coal, as given in the above table, yielded 0.30 per cent sulfide sulfur in the coke. After hydrochloric acid extraction of the coal, the coke still contained 0.31 per cent, and even after the further extraction with phenol, the coke showed 0.27 per cent sul-



fide sulfur. It would appear from these results that the origin of the sulfide sulfur of the coke was elsewhere than in the sulfate or resinic sulfur. In all probability it comes entirely from the iron pyrites.

### Conclusions

First. It is very probable from this investigation that the sulfur forms of the coals change as follows when the coal is coked.

(a) The sulfate sulfur is retained by the coke but in some other form than inorganic sulfate.

(b) The pyritic sulfur is partially volatilized and a portion is also left in the coke, probably as sulfide sulfur. All of the pyrites are decomposed.

(c) The resinic sulfur is mostly left in the coke, but in that in which a different form than <sup>it</sup> existed in the coal.

(d) The humus sulfur volatilizes partly but some is left in the coke in a changed form.

Second. The forms of sulfur in the coke were studied, but were not fully identified. A small part of the sulfur exists as sulfide, but the combination of the rest is unknown as yet. This unknown form is extremely stable to strong acids, oxidizing agents, and heat. It gives off hydrogen sulfide on treatment with nascent hydrogen or, when red hot, with water.

Third. During the coking process, secondary reactions between constituents of the coal and decomposed sulfur compounds enter into the question of the quantity of sulfur retained by the coke.

Fourth. The further study of sulfur changes during coking and particularly the study of the coke sulfur compounds themselves is important.







### General Summary

The following is a brief resumé of the points studied and the results obtained in the present investigation.

1. The sulfur in coal has been found to be present in four forms:- sulfate sulfur, the sulfur of iron pyrites, and two organic types, namely, resinic sulfur and humus sulfur.

2. A scheme of analysis has been devised for determining each of the four forms.

3. The gradual oxidation of the sulfur to the sulfate form has been found to proceed independently, to a certain extent, of the amount of free oxygen present.

4. The changes in the forms of coal sulfur during coking have been studied. The sulfur of coke consists of sulfide sulfur and another form in very stable combination, probably with carbon.



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"The Effect of Certain Organic Compounds on Wheat Plants In the Soil", Journal of Industrial and Engineering Chemistry. Vol. 7, p. 420 (1915).

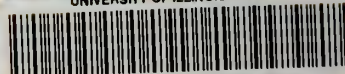
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